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SECTION A.—MATHEMATICAL AND PHYSICAL SCIENCES.

BAKERIAN LECTURE:—*Rays of Positive Electricity.*

By Prof. Sir J. J. THOMSON, O.M., F.R.S.

(Lecture delivered May 22,—MS. received June 4, 1913.)

[PLATES 1—3.]

In 1886, Goldstein observed that when the cathode in a vacuum tube was pierced with holes, the electrical discharge did not stop at the cathode; behind the cathode, beams of light could be seen streaming through the holes in the way represented in fig. 1. He ascribed these pencils of light to rays passing through the holes into the gas behind the cathode; and from their association with the channels through the cathode he called these rays Kanalstrahlen. The colour of the light behind the cathode depends upon the gas in the tube: with air the light is yellowish, with hydrogen rose colour, with neon the gorgeous neon red, the effects with this gas being exceedingly striking. The rays produce phosphorescence when they strike against the

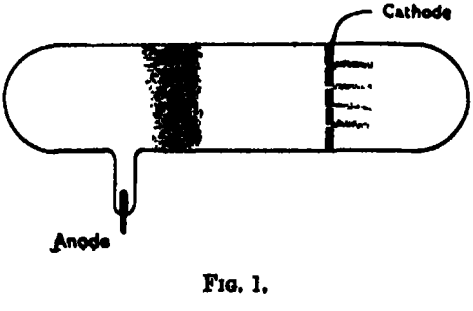

FIG. 1.

walls of the tube; they also affect a photographic plate. Goldstein could not detect any deflection when a permanent magnet was held near the rays. In 1898, however, W. Wien, by the use of very powerful magnetic fields, deflected these rays and showed that some of them were positively charged; by measuring the electric and magnetic deflections he proved that the masses of the particles in these rays were comparable with the masses of atoms of hydrogen, and thus were more than a thousand times the mass of a particle in the cathode ray. The composition of these positive rays is much more complex than that of the cathode rays, for whereas the particles in the cathode rays are all of the same kind, there are in the positive rays many different kinds of particles. We can, however, by the following method sort these particles out, determine what kind of particles are present, and the velocities with which they are moving. Suppose that a pencil of these rays is moving parallel to the axis of x, striking a plane at right angles to their path at the point O; if before they reach the plane they are acted on by an electric force parallel to the axis of y, the spot where a particle strikes the plane will be deflected parallel to y through a distance y given by the equation

$$y = \frac{e}{mv^2}\text{A},$$

where e, m, v, are respectively the charge, mass, and velocity of the particle, and A a constant depending upon the strength of the electric field and the length of path of the particle, but quite independent of e, m, or v.

If the particle is acted upon by a magnetic force parallel to the axis of y, it will be deflected parallel to the axis of z, and the deflection in this direction of the spot where the particle strikes the plane will be given by the equation

$$z = \frac{e}{mv}\text{B},$$

where B is a quantity depending on the magnetic field and length of path of the particle, but independent of e, m, v. If the particle is acted on simultaneously by the electric and magnetic forces, the spot where it strikes the plane will, if the undeflected position be taken as origin, have for co-ordinates

$$x = 0, \qquad y = \frac{e}{mv^2}\text{A}, \qquad z = \frac{e}{mv}\text{B}. \tag{1}$$

Thus no two particles will strike the plane in the same place, unless they have the same value of v and also the same value of e/m; we see, too, that if we know the value of y and z, we can, from equation (1), calculate the values of v and e/m, and thus find the velocities and character of the particles composing the positive rays.

From equation (1) we see that

$$z^2 = \frac{e}{m} y \frac{B^2}{A}, \qquad z = y \, . \, v \frac{B}{A}. \tag{2}$$

Thus all the particles which have a given value of e/m strike the plane on a parabola, which can be photographed by allowing the particles to fall on a photographic plate. Each type of particle in the positive rays will produce a separate parabola, so that an inspection of the plate shows at a glance how many kinds of particles there are in the rays; the measurement of the parabolas, and the use of equation (2), enables us to find the values of m/e corresponding to them, and thus to make a complete analysis of the gases in the positive rays. To compare the values of m/e corresponding to the different parabolas, we need only measure the values of z on these parabolas corresponding to a constant value of y. We see from equation (2) that the values of e/m are proportional to the squares of the values of z. Thus, if we know the value of e/m for one parabola, we can with very little labour deduce the values of e/m for all the others. As the parabola corresponding to the hydrogen atom is found on practically all the plates, and as this can be at once recognised, since it is always the most deflected parabola, it is a very easy matter to find the values of m/e for the other particles. Photographs made by the positive rays after they have suffered electric and magnetic deflections are reproduced in figs. 2 and 3 (Plate 1). The apparatus I have used for photographing the rays is shown in fig. 4.

A is a large bulb of from 1 to 2 litres capacity in which the discharge passes, C the cathode placed in the neck of the bulb. The position of the front of the cathode in the bulb and the shape of the bulb where it joins the neck D have a very considerable influence on the brightness of the rays and the distribution of velocities among the particles. If the cathode projects into the bulb, the pressure of the gas in the bulb when the rays are the brightest is apt to be inconveniently low, and the same is true when,

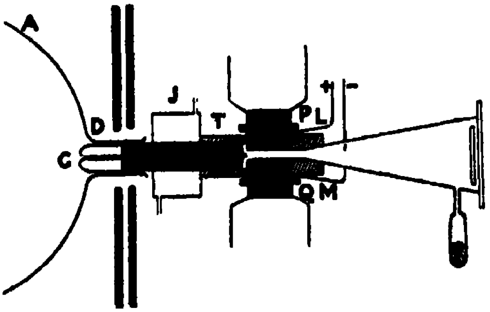

FIG. 4.

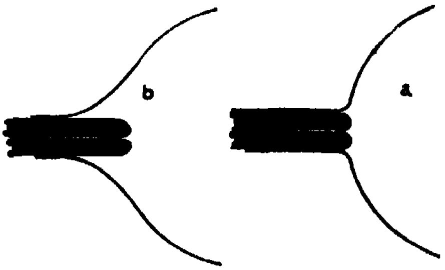

FIG. 5.

though the cathode is kept in the neck, the bulb swells out gradually from the neck instead of starting off abruptly. I have got the best results by making the transition from the neck to the bulb as abrupt as possible and putting the front of the cathode flush with the junction of the neck and the bulb, in the way shown in fig. 5*a*; this gives better results than when the cathode is placed as in fig. 5*b*.

The form of cathode which I have found to give the best pencil of rays is shown in fig. 4. The front of the cathode is an aluminium cap, carefully worked so as to be symmetrical about an axis: this cap fits on to a cylinder made of soft iron with a hole bored along the axis; the object of making the cathode of iron is to screen the rays from magnetic force while they are passing through the hole. A case fitting tightly into this hole contains a long narrow tube which is the channel through which the rays pass into the tube behind the cathode. This tube is the critical part of the apparatus, and failure to obtain a good pencil of rays is generally due to some defect here. As the length of this tube is very long in proportion to its diameter—the length of most of the tubes I have used is about 6 cm. and the diameter from 0·1 to 0·5 mm.—it requires considerable care to get it straight enough to allow an uninterrupted passage to the rays. The method we use is to start with a piece of fine copper tubing and draw it out until the diameter is reduced to the right value, the proper length is cut off, and this is rolled between two surface plates, until optical examination shows that it lets a pencil of light pass without obstruction through the tube; it is useless to attempt to experiment with positive rays unless this tube is exceedingly straight. The rays themselves exert a sand blast kind of action on the tube and disintegrate the metal; after prolonged use the metallic dust may accumulate to such an extent that the tube gets silted up, and obstructs the passage of the rays. The cathode is fixed into the glass vessel by a little wax; the joint is made tight so that the only channel of communication from one side of the cathode to the other is through the tube in the cathode. The wax joint is surrounded by a water jacket J to prevent the wax being heated by the discharge. The arrangements used to produce the electric and magnetic fields to deflect the rays are shown at L and M. An ebonite tube is turned so as to have the shape shown in fig. 4, L and M are two pieces of soft iron with carefully worked plane faces, placed so as to be parallel to each other, these are connected with a battery of storage cells and furnish the electric field. P and Q are the poles of an electromagnet separated from L and M by the thin walls of the ebonite box: when the electromagnet is in action there is a strong magnetic field between L and M; the lines of magnetic force and electric force are by this arrangement parallel to each other and the electric and magnetic fields are as nearly as possible coterminous. This arrangement was adopted for a special investigation in which it was desirable that the two fields should not overlap; for many purposes, for example, the analysis of the gases in the tube, this condition is not important, and the simpler arrangement shown in fig. 6 answers all the requirements. Here the ebonite box is done away with, the electric field is produced between two parallel plates of metal, P_1, P_2, and the magnetic field is produced by an electromagnet whose poles are on opposite sides of the tube. The arrangement used for photographing the rays is that designed by Mr. Aston and described in the 'Phil. Mag.,' 1911, vol. 21, p. 227. Plates of soft iron are placed between the electromagnet and the discharge tube to prevent the discharge from being affected by the magnetic field.

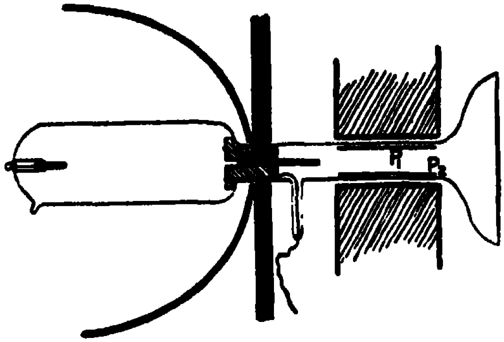

Fig. 6.

The pressure in the tube behind the cathode must be kept very low, this is done by means of a tube containing charcoal cooled by liquid air. The pressure on the other side of the cathode is much higher.

A typical photograph taken with this apparatus is reproduced in fig. 7.

It will be noticed that in addition to the parabolic arcs whose origin has already been discussed, there are a series of lines approximately straight. These secondary lines are due to particles which have been charged for a part only of the time they were in the electric and magnetic fields and are therefore not so much deflected as those which were charged for the whole time and which produce the parabolas. Some particles which are charged when they enter those fields lose their charges before they get through, while others which are uncharged to begin with gain a charge before they leave the fields. We can distinguish between these cases in the following way. Make the magnetic field M (fig. 8) overlap the electric field E, so that in the region EM the particles are exposed to magnetic but not to electric forces.

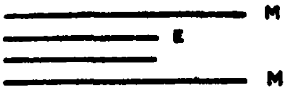

Fig. 8.

A particle which begins by being uncharged and first picks up a charge in this region will experience a magnetic without an electric deflection, so that the trace made on the photograph by the particles which pick up a charge will resemble fig. 9, *a*.

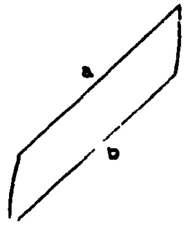

Fig. 9.

Now, consider the trace made by the particles which started with a charge but lost it before they got through: these, when they are in the region EM, will have already experienced a considerable deflection so that the place where they get a magnetic without an electric deflection will be at the most deflected end of the line and the shape of the trace they make on the plate will be somewhat like fig. 9, *b*. An example of this effect is shown in the photograph reproduced in fig. 10.

Unless the pressure in the observation chamber is very low, few of the particles remain charged during the whole of the journey through the electrostatic and magnetic fields, and in this case the parabolas disappear, and only the lines due to the secondaries appear on the plate.

The parabolas are determined by the values of e/m, thus an atom with a single charge would produce the same parabola as a diatomic molecule with a double charge. We can, however, by the following method distinguish between parabolas due to particles with a single charge and those due to particles with more than one charge.

The parabolas are not complete parabolas, but arcs starting at a finite distance from the vertical, this distance is by equation (1) inversely proportional to the maximum kinetic energy possessed by the particle. This maximum kinetic energy is that due to the charge on the particle falling from the potential of the anode to that of the cathode in the discharge tube. Consider now the particles which have two charges: these acquire in the discharge tube twice as much kinetic energy as the particles with a single charge. Some of these doubly charged particles will lose one of their charges while passing through the long narrow tube in the cathode, and will emerge as particles with a single charge; they will, however, possess twice as much kinetic energy as those which have had one charge all the time. Thus the stream of singly charged particles emerging from the tube will consist of two sets, one having twice as much kinetic energy as the other; the particles having twice the kinetic energy will strike the plate nearer to the vertical than the others, and will thus prolong beyond the normal length the arc of the parabola corresponding to the singly charged particle. An example of this is shown in the photograph reproduced in fig. 11, where the line α, due to a singly charged oxygen atom for which $m/e = 16$, is prolonged until its extremity is only half the normal distance from the vertical. The line β on the photograph gives $m/e = 8$, hence we conclude that this line is due to an atom of oxygen with two charges, whereas if the oxygen line had not been prolonged we should have concluded that β was due to a singly charged atom with an atomic weight 8.

If the atom acquired more than two charges the prolongation of the atomic line would be still longer. If, for example, it could acquire eight charges it would be prolonged until its extremity was only one-eighth of the normal distance from the vertical. An example of this is shown in fig. 12 (Plate 2), where α is the line due to the singly charged mercury atom, this approaches to within one-eighth of the normal distance, and the theory is verified by the appearance on the plate of the lines β, γ, δ, ..., which correspond to mercury atoms with 2, 3, 4, 5, 6, 7 charges. The lines due to the one with 8 charges cannot be detected, but the intensity of the lines diminishes as the charge increases, and it is perhaps legitimate to conclude that with more sensitive apparatus the line corresponding to the atom with eight charges might be detected.

Using this method to distinguish between singly and multiply charged systems we find that the particles which produce the parabolas on the photographic plates may be divided into the following classes:—

1. Positively electrified atoms with one charge.
2. Positively electrified molecules with one charge.
3. Positively electrified atoms with multiple charges.
4. Negatively electrified atoms.
5. Negatively electrified molecules.

The production of a charged molecule involves nothing more than the detachment of a corpuscle from the molecule, that of a charged atom requires the dissociation of the molecule as well as the electrification of the atom. As the results are so different we naturally ask, Is the mechanism by which the charged atoms are produced the same as that which produces the charged molecules? There seems to me to be strong evidence that the charged atoms and molecules are produced by different agents. We not infrequently find that some of the parabolas have characteristic peculiarities such as abrupt changes in intensity. An example of this is shown in figs. 13 and 13A, where several of the lines broaden abruptly at points which are all in the same vertical line, showing that the particles where the broadening commences have all the same kinetic energy. This indicates that at certain places in the discharge tube there is an abnormally large production of the particles corresponding to these parabolas. It will be noticed, however, that it is only some of the parabolas which show this effect, there are others which are of approximately the same intensity throughout. The measurement of the parabolas shows that the uniform ones correspond to atoms while those with the swellings correspond to molecules. Thus we may at certain places in the dark space have great changes in the production of charged molecules without any change in the production of charged atoms. This proves, I think, that the two are produced by different agencies.

Another argument in favour of this view is the great variation that occurs in the relative intensities of the lines due to the atoms and molecules of the same element when the conditions of discharge are slightly altered. I will confine myself to the case of the lines due to the atoms and molecules of hydrogen. By altering the position of the cathode in the neck of the discharge tube we can make the line due to the atom either more or less intense than that due to the molecule. Thus if the cathode is well inside the neck the line due to the atom is more intense than that due to the molecule, while if the cathode is pushed forward into the bulb the line due to the molecule is more intense than that due to the atom. Examples of this difference are shown in figs. 14 and 15. These changes in the position of the cathode involve changes in the pressure of the gas, for to get the positive rays well developed the pressure has to be higher when the cathode is in the neck than when it protrudes into the bulb, so that it would seem that reduction of pressure favours the formation of charged molecules more than that of charged atoms.

In the discharge tube we have cathode rays, positively electrified atoms and molecules, and rays analogous to soft Röntgen rays; all these are known to ionise a gas when they pass through it. As far as my observations have gone the properties of the positive rays indicate that the cathode particles produce the positively charged molecules, while the moving positively electrified particles produce the positively electrified atoms. I do not mean by this that under no circumstances can a cathode particle produce a positively charged atom, for it would probably do so if it struck one of the structural corpuscles, *i.e.* one of those which bind the two atoms in the molecule together. The number of molecules struck in this way would, however, be only a small fraction of those struck by the rays, so that if this were the only source of ionisation the number of charged atoms would be small compared with that of charged molecules. This, however, is not the case, so that we conclude that moving positively charged atoms and molecules are in the main responsible for the dissociation which produces the positively charged atoms occurring in the positive rays.

I will now pass on to the consideration of another very interesting type of positive ray—the multiply charged atom. I say atom advisedly, because it is doubtful whether we get among the positive rays multiply charged molecules. The indication of a multiple charge is that the line corresponding to the singly charged carrier is prolonged abnormally towards the vertical. The only case of a line due to a molecule for which I have observed a suspicion of such a prolongation is that of the line for which $m/e = 28$, corresponding to a molecule of nitrogen or carbon monoxide. There is reason for doubting whether this is a genuine prolongation of the molecular line, as, since m/e for aluminium = 27·3, if any aluminium atoms from the cathode got into the discharge tube, the prolongation might be that of the atomic line of aluminium rather than that of the line due to the molecule of nitrogen.

The rarity of the doubly charged molecule seems to indicate that the shock which produces the double charge is sufficiently intense to dissociate the molecule into its atoms. The uniformity of the intensity of the parabolas corresponding to the multiply charged atoms shows that they acquire this charge at one operation and not by repeated ionisation on their way to the cathode.

The occurrence of the multiple charge does not seem to be connected with the valency or other chemical property of the atom. Of all the elements whose lines I have studied, hydrogen and X_3 (see p. 14) are the only ones which have never appeared with a double charge. Elements as different in their chemical properties as carbon, nitrogen, oxygen, chlorine, helium, neon, a new gas whose atomic weight is 22, argon, crypton, mercury, all give multiply charged atoms. The fact that these multiple charges so frequently occur on atoms of the inert gases proves, I think, that they are not produced by any process of chemical combination.

All the results point to the conclusion that the occurrence and magnitude of the multiple charge is connected with the mass of the atom rather than with its valency or chemical properties. We find, for example, that the atom of mercury, the heaviest atom I have tested, can have as many as 8 charges, crypton can have as many as 5, argon 3, neon 2, and so on. There is evidence that when these multiple charges occur the process of ionisation is generally such that the atom starts either with one charge or with the maximum number, that in the ionisation of mercury vapour, for example, the mercury atom begins either with 1 charge or with 8, and that the particles which produce the parabola corresponding to 5 charges, for example, started with 8 and lost 3 of them on its way through the tube in the cathode. The intensity of the lines corresponding to multiply charged atoms varies greatly with what are apparently but small alterations in the condition of the discharge, a slight alteration in the pressure or in the position of the cathode may make all the difference between the lines being quite strong or so faint as to be hardly visible.

We shall now pass on to consider the negatively electrified particles which are found mixed with the positive rays. These have much the same energy as the positively electrified ones; they are, in fact, positively electrified until they reach the cathode, they get neutralised after passing through it, and attract another corpuscle, thus getting negatively electrified before reaching the electric and magnetic fields. As they are moving past the corpuscles at a very high speed, in some cases as fast as 2×10^8 cm./sec., it is evident that their attraction for the corpuscles must be very considerable, otherwise they could not grip and hold fast a corpuscle under such conditions. The power of a particle to get negatively electrified may thus be taken as an indication of the strength of the electric field round it, if the electric field is small, *i.e.* if the chemical affinities of the particle are saturated, it will not be able to pick up a corpuscle and become negatively electrified, while it may be able to do so if it is unsaturated and the electric field around it intense.

Now I have not yet found a case where a molecule of a compound gas acquires a negative charge, and only two cases, which will be considered later on, where a molecule of an elementary gas does so. Again, there are some elements whose atoms, when in the positive rays, never acquire a negative charge, such as nitrogen, helium, neon, argon, crypton, and mercury vapour, while negative charges are found on the atoms of hydrogen, carbon, oxygen, sulphur, chlorine. In oxygen the parabolas due to the negatively charged atoms are exceptionally strong; an example of this is shown in the photograph reproduced in fig. 11, which was taken when the gas in the discharge tube was very pure oxygen. Another photograph, showing the lines due to negatively electrified oxygen and carbon atoms, is reproduced in fig. 16.

The two cases where I have found a molecule of an element to be negatively charged are oxygen and carbon. The negatively electrified molecule of oxygen does sometimes occur, although it is by no means common; the conditions for its appearance have not been worked out with certainty, it is probably connected with the presence in the discharge tube of some oxygen compounds of a special type; the negatively charged oxygen atom, on the other hand, occurs in nearly every case when oxygen is present in the tube. It is not perhaps inconsistent with the chemical properties of oxygen to suppose that in some compounds we may have two oxygen atoms united together so as to form a system with a good deal of residual affinity, hydrogen peroxide is perhaps an example of this.

The conditions which regulate the appearance of the negatively charged carbon molecule have been worked out and are very interesting. The negative molecule does not occur in compounds like marsh-gas, carbon dioxide, carbon monoxide, phosgene, and so on, where there is no linking between carbon atoms. On the other hand, it does occur with compounds like acetylene, ethylene, ethane, where there are two carbon atoms linked together by one or more bonds. This is interesting from the chemical point of view because it shows that in such compounds two carbon atoms are held so firmly together that they remain united when the molecule is broken up by the rough treatment it receives in the discharge tube; and secondly, that the system consisting of the two carbon atoms is a highly unsaturated one, as there is an electric field round it strong enough to catch and hold a corpuscle moving past it at a very high speed. In benzene vapour we get negatively electrified triplets of carbon atoms, and I have sometimes thought that I could detect the negative quartet.

The Use of Positive Rays as a Method of Chemical Analysis.

Since each parabola on the photograph indicates the presence in the discharge tube of particles having a known value of m/e, and as by the methods described above we can determine what multiple e is of the unit charge, we can, by measuring the parabolas, determine the masses of all the particles in the tube, and thus identify the contents of the tube as far as this can be done by a knowledge of the atomic and molecular weights of all its constituents. The photograph of the positive rays thus gives a catalogue of the atomic and molecular weights of the elements and compounds in the tube. This method has several advantages in comparison with that of spectrum analysis, especially for the detection of new substances; for, with this method, when we find a new line we know at once the atomic or molecular weight of the particle which produced it. Spectrum analysis would be much easier and more efficient if from the wave-length of a line in the spectrum we could deduce the atomic weight of the element which produced it, and this virtually is what we can do with the positive-ray method.

Again, in a mixture the presence of one gas is apt to swamp the spectrum of another, necessitating, in many cases, considerable purification of the gas before it can be analysed by the spectroscope. This is not the case to anything like the same extent with the positive rays; with these the presence of other gases is a matter of comparatively little importance.

With regard to the sensitiveness of the positive ray method, I have made, as yet, no attempt to design tubes which would give the maximum sensitiveness, but with the tubes actually in use there is no difficulty in detecting the helium contained in a cubic centimetre of air, even though it is mixed with other gases, and I have not the slightest doubt a very much greater degree of sensitiveness could be obtained without much difficulty.

I will illustrate the use of the method by some applications. The first of these is to the detection of rare gases in the atmosphere. Sir James Dewar kindly supplied me with some gases obtained from the residues of liquid air; the first sample had been treated so as to contain the heavier constituents. The positive-ray photograph reproduced in fig. 17 gave the lines of xenon, crypton, argon, and a faint line due to neon; there were no lines on the photograph unaccounted for, and so we may conclude that there are no heavy unknown gases in the atmosphere occurring in quantities comparable with that of xenon. The second sample from Sir James Dewar contained the lighter gases; the photograph (fig. 18) shows that, in addition to helium and neon, there is another gas with an atomic weight about 22. This gas has been found in every specimen of neon which has been examined, including a very carefully purified sample prepared by Mr. E. W. Watson and a specimen very kindly supplied by M. Claud, of Paris; the photograph of this specimen, fig. 19 (Plate 3), is remarkable, as it shows, in addition to this line and the helium line, a line corresponding to a substance with atomic weight 3, whose properties are discussed later on. The substance giving the line 22 also occurs with a double charge, giving a line for which $m/e = 11$. There can, therefore, I think, be little doubt that what has been called neon is not a simple gas but a mixture of two gases, one of which has an atomic weight about 20 and the other about 22. The parabola due to the heavier gas is always much fainter than that due to the lighter, so that probably the heavier gas forms only a small percentage of the mixture.

Another application of the method was to the analysis of the gas in a small glass tube in which 30 mgrm. of radium bromide had been sealed for more than 10 years. The photograph showed that, in addition to helium, the tube contained considerable quantities of neon, or some gas with about the same atomic weight, some gas of the atomic weight 3 mentioned before, and also a trace of argon, a little more than I should have expected from the volume of air in the tube, although the difference was not very great. The photograph is shown in fig. 20.

The last application of the method I shall bring before you is to the investigation of the gas for which $m/e = 3$. The most convenient way of producing this gas is by bombarding solids by cathode rays. The arrangement used for this purpose is shown in fig. 21. A is a vessel communicating by a tube with the bulb B, in which the positive rays are produced; a tap is placed in the tube, so that the communication between the vessels can be cut off if desired. A is provided with a curved cathode, like those used for Röntgen-ray focus tubes, and the cathode rays focus on the platform on which the substance to be bombarded is placed. After the solid to be examined has been placed on the platform, the tap between A and B is turned so as to cut

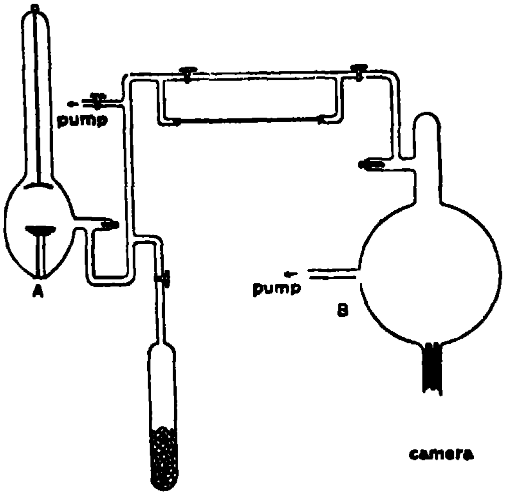

Fig. 21.

off the connection between them, A is exhausted until the pressure is low enough for the cathode rays to be produced, the electric discharge is sent through A, and the cathode rays bombard the solid; the result of this is that in a very short time so much gas, mainly CO_2 and hydrogen, is driven out of the solid that the pressure gets too high for the cathode rays to be formed; to reduce the pressure a tube containing charcoal cooled by liquid air is connected with A, and the gases given off at the commencement of the bombardment are absorbed by the charcoal; after the first rush of gas has come off, the charcoal is cut off from A by the tap.

To analyse the gases given off from the solid, a photograph is taken before the connection between A and B has been opened; after this is finished and when the bombardment has been going on for some hours, the tap is turned and a little of the gas from A is allowed to go into B: another photograph is taken, and the lines in the second photograph which are not in the first represent the gases which have been liberated by the bombardment. The solids tested include platinum, lead (both old and some chemically pure, procured from Kahlbaum), gold, silver, copper, iron, nickel, nickel oxide, zinc, aluminium, magnesium, uranium, palladium, graphite, calcium carbide, diamond dust, mica, lithium chloride, potash, potassium iodide, potassium chloride, fluorspar, two specimens of meteorites, monazite sand, volcanic dust. In every case, except the two last, a gas whose atomic weight is 3 was found to have been liberated by the bombardment with cathode rays; in some cases the parabola corresponding to it was very well marked, as in the photograph reproduced in fig. 22, which is taken with the gas driven out of platinum (the X_3 line is the third from the top); of the substances tried, the line corresponding to the gas with atomic weight 3, which I shall denote henceforth by X_3, was strongest with platinum, lithium chloride, and potash. The gas continues to come off, even though the bombardment is prolonged for some hours, but in all the cases I have tried it ceases if the bombardment is prolonged for the working hours of several days, and the metal arrives at a state when it can be bombarded without liberating the X_3. The metal before bombardment can be heated to a high temperature without producing much diminution in the supply of this gas given off under the cathode rays, but by heating copper gauze, made of very fine wire, in a vacuum in a quartz tube to a red heat for about 40 hours it was reduced to a state when it no longer gave off X_3 under bombardment.

Helium and in some cases neon or a gas with approximately the same atomic weight are given off along with the X_3 when solids are bombarded by cathode rays. Almost every substance I have bombarded gives off sufficient helium to be detected by this method. After long bombardment, however, the supply of helium gives out, generally long before the X_3 is exhausted. This is hardly to be wondered at, for in most cases the amount of X_3 is much greater than that of helium. In minerals like thorianite, monazite, the two meteorites I examined, and a specimen of volcanic dust, the helium is in excess, in monazite and thorianite the X_3 is but a small fraction of the helium. This method is a very convenient one for analysing the gases in minerals. I may say in passing that helium in small quantities is by no means an infrequent impurity in gases. I have detected it as well as X_3 in some oxygen obtained from a cylinder. I do not mean, however, to imply that all such oxygen contains helium.

With regard to the origin of the gases given out on bombardment, the fact that the emission of gas ceases after prolonged bombardment, and that thin copper wire by long continued heating can be brought to a state in which it ceases to emit the gas, favours the conclusion that in such cases the gas is originally present in the solid, or at any rate is not manufactured *de novo* by the action of the cathode rays alone. The question arises, Are the gases merely absorbed by the solid in the same way that air is absorbed by water or are they constituents of atoms or molécules which are decomposed by the cathode rays? The gas is certainly held with surprising firmness by the metal, the only case in which I have been able to get rid of it by heating is that of the fine copper wire heated to redness for a week. I have heated lead in a vacuum until two-thirds of it were boiled away and yet the remainder still gave off some helium and X_3 when bombarded by the cathode rays. I tested the gases given out from the lead when heated and found traces of X_3 and also of helium; the quantities obtained in this way were, however, very small compared with those produced by bombardment with cathode rays.

If the gases were absorbed in the solids we should expect to be able to eliminate them by dissolving the solid in water or acid and evaporating the solution to dryness; in some cases, however, this treatment does not reduce the quantity of gas liberated by the cathode rays. A conspicuous instance is lithium chloride: a sample of this when bombarded gave off X_3 and helium, it was then dissolved in water and the solution evaporated to dryness, the freshly deposited lithium chloride gave off X_3 and helium as freely as it did before solution, indeed the helium line seemed to be stronger than before. This process was repeated nine times without leading to any diminution in the gases given out. Similar results are obtained when the LiCl is dissolved in alcohol instead of water and when KHO is substituted for LiCl. It would seem very improbable that any gas merely absorbed or imprisoned by the solid would have been able to withstand this treatment, which, however, would not have eliminated any soluble compound of these gases. This persistence after solution suggests that the gas is in a state of chemical combination and is not merely absorbed in the usual meaning of the term. We shall see that the gas X_3 has some power of entering into chemical combination so that the existence of it as a compound is not impossible. The lithium chloride, however, gives off helium after solution, as well as X_3, so that, assuming that the solution and subsequent heating would eliminate any helium in the free state, the helium must either be generated from LiCl by the bombardment of the cathode rays, or else it must exist in some compound sufficiently stable to admit of being dissolved without decomposition.

In some cases, though not as we have seen in all, solution has the effect of putting the metal into a state in which it does not give off either X_3 or helium when bombarded. Thus I could get no gas from lead freshly deposited as a "lead tree"; again, iron which gave off gas when bombarded ceased to do so when dissolved and re-precipitated. Again, platinum dissolved up in acid and converted into spongy platinum five times in succession, though it did not altogether cease to give off gas under bombardment, did not emit anything like so much as it did before bombardment. The differences in the effects produced by the solution of the metal in different cases would be readily intelligible if these gases formed compounds of different qualities with the different metals.

Though the largest quantities of X_3 are obtained by bombardment with cathode rays, this is by no means the only source of the gas. It and helium are obtained when the discharge from a Wehnelt cathode passes through an exhausted tube. Indeed I had observed the line corresponding to it on several occasions on the photographic plate long before I tried bombarding the solids; its appearance was, however, very sporadic and although I tested a great variety of gases I was never able to get it at will until after a tedious search I hit upon the method of bombarding solids.

I will now pass on to describe the experiments I have made to test the nature of the substance X_3.

The most obvious suggestion is that it is a carbon atom with four charges of electricity. This, however, is not tenable, for the following reasons. The first are based on physical principles. We have seen that a multiply charged atom involves a prolongation of the line due to the singly charged one; in the case of an atom with four charges the primary line would be prolonged until it reached up to one-quarter of the normal distance from the vertical. Now I have never observed a prolongation of the line due to the carbon atom beyond the half distance, this corresponds to a doubly charged atom, and the line for this atom is frequently found on the plate, though always fainter than the primary line. Again, on many of the plates where the X_3 line is strongest there is no prolongation of the line due to the carbon atom at all, and no line corresponding to the doubly charged atom. In some cases, indeed, the X_3 line is stronger than the primary carbon line, and in all cases when the gas is generated by bombardment stronger than the doubly charged carbon line. This is the argument from the physical side; there is, however, another argument based on consideration of a chemical character. The gas X_3 can be stored and tested weeks after the bombardment has taken place. If then the line is due to the carbon atom with four charges it must be that some carbon compound is produced by the bombardment which, when introduced into the discharge tube, gives a plentiful supply of carbon atoms with four charges. Now I have put directly into the tube all the gaseous carbon compounds I could get, including marsh-gas, carbon dioxide, carbon monoxide, carbon tetrachloride, phosgene gas, carbon bisulphide, cyanogen, acetylene, ethylene, ethane, the vapours of a number of alcohols and ether, benzene, coal gas, without getting a trace of the X_3 line. Again, X_3 can resist treatment with hot copper oxide and potash, which would remove the carbon compounds. For these reasons we may, I think, put aside the idea that X_3 is due to carbon.

If X_3 does not contain a new element and is not carbon with four charges it must be triatomic hydrogen. From the physical side there is considerable evidence in favour of this view; for example, whenever X_3 is freely produced by bombardment, it is always accompanied by large quantities of hydrogen: we may, however, have large quantities of hydrogen without X_3. The chemical properties of X_3, however, in no way suggest hydrogen, so that if it is manufactured from that gas its relations to hydrogen must be very different from those of ozone to oxygen. The properties of X_3 brought to light by these experiments are as follows:—

It can be kept over mercury for several weeks, although it is diminished in amount at the end of that time.

It can be heated in a quartz tube for several hours without any appreciable change, although the quartz is at a red heat.

It can be sparked with oxygen and also with phosphorus without being destroyed.

It is not affected when passed over cold metallic sodium, and when heated with sodium vapour it does not combine with it.

It can withstand the action of red-hot copper oxide and potash. This experiment was tried seven times, in two cases there was an appreciable diminution in the quantity of X_3, in the others there was no effect. The exceptional cases, I am inclined to think, were due to some of the copper being reduced, as hot copper combines, to some extent, with X_3. Fig. 23 (3) is from a photograph when the gas had passed over hot copper oxide; 23 (2) and (4) of the same gas which had not been treated. 23 (1) is the check taken before the gas was admitted; it does not show the 3′ line or the helium, which would come just under the strong line at the top, which is due to the hydrogen molecule.

It can stand over potash for several days without being absorbed

These properties point to its being a very inert substance, and are not those we should expect an allotropic form of hydrogen to possess. I have found, however, two cases where it enters into chemical combination—

(1) It combines with mercury vapour when an electric discharge is sent through the mixture.

(2) It combines, to some extent, with red-hot copper. This is illustrated by the photograph reproduced in fig. 24; (1) is the check before introducing the gas, (2) and (4) that of gas not passed over copper; (3) that of the gas after passing the copper, in this the 3′ line is fainter than in (2) and (4).

These properties point to the conclusion that if X_3 is an element it has considerable resemblance to the inert gases helium and argon, although its chemical properties are slightly more energetic. The absence of parabolas corresponding to $m/e = 1{\cdot}5$ and $m/e = 6$ shows that if it is an element it is monatomic. Mendeléeff predicted the existence of an element of atomic weight 3, and attributed to it properties similar to those of fluorine, but of greater intensity. The chemical properties of X_3 are much too lethargic to be consistent with the view that it is a kind of super-fluorine. If X_3 is related to such an element, that element must have an atomic weight 2 and not 3, and X_3 must be a stable compound of it with hydrogen. If this were the case, since the line corresponding to the element would coincide with that due to the hydrogen molecule, which is always on the plate, it would be difficult to get, by the study of the lines due to the positively charged particles, evidence as to its existence. We should expect, however, that a substance possessing the energetic chemical properties of Mendeléeff's element would be able to attract a negative charge, and that there would be on the negative side of the photographs a line for which $m/e = 2$. I have not, however, as yet been able to detect the existence of such a line. Again, with but three exceptions, H, B, N, all the atomic weights less than 40 are of the form $4n$ or $4n+3$; if the atomic weight of X_3 were 2 it would be another exception to this law.

I have much pleasure in thanking Mr. F. W. Aston, B.A., of Trinity College, and Mr. E. Everett, for the invaluable assistance they have given me with these experiments.

[*Note added June* 14, 1913.—In the experiments described in the lecture the evolution of X_3 and helium from metals under bombardment by cathode rays was in most cases much smaller when the metals had been freshly deposited, and the solution evaporated to dryness, than it was with metals which had not been so treated. The supply of helium, too, soon gave out under bombardment, indicating that the helium had been absorbed by the metal and was liberated by the bombardment. There was one case, however, that of LiCl, in which solution produced no diminution in the amount of helium given out. This result led me to examine within the last few days the effect of bombarding by cathode rays the salts of the alkali metals and of the alkaline earths; these experiments have convinced me that when the salts of Li, Na, K or Rb are bombarded by cathode rays there is a genuine production, as distinct from liberation of absorbed gas, of helium and X_3, potassium giving the largest supply. The amount of helium obtained from these elements was much larger than that from any of the substances I have tried other than minerals such as monazite sand, thorianite, volcanic ash, or meteorites, which are known to contain free helium. On the other hand, the salts of calcium, ammonium, and silver, have shown no special power of giving out helium; the very small amount obtained was not more than could be accounted for by absorbed gas, they produce X_3, however, quite freely.

The advantage of using the salts instead of the metals themselves is that, by solution in water or alcohol and subsequent evaporation to dryness, they can be freed from absorbed helium and X_3. The salts examined were LiCl, LiOH, Li_2CO_3, NaCl, KHO, KI, KCl, RbI, NH_4Cl, $CaCl_2$, CaO (this was a portion of a lime-light cylinder), and AgCl. The lithium, sodium, potassium, and rubidium salts showed the helium line strongly, especially the potassium salts; indeed, except with minerals which are known to contain helium, I have never seen the helium line so strong as it was when KI was bombarded. The strength of the He line was not diminished by repeated solution and evaporation; on the contrary, it was increased sometimes to a considerable extent. I think this increase may be a secondary effect, due to the elimination from the salt of the ordinary absorbed gases, such as H_2 and CO_2. The result of this is that a smaller amount of gas comes off when the salt is bombarded, the pressure in the bombardment chamber is lower, and the cathode rays are faster and more energetic. The helium did not come from the electrodes, for when CaO or AgCl was bombarded with the same electrodes, at the same pressure and for the same time, little or no helium was produced. As an additional precaution, the cathode was scraped from time to time. All the samples of the salts I have tried give the same results. This makes it improbable that the effects are due to the presence of some helium-containing mineral like monazite sand. I have dissolved some of the salts in alcohol, and filtered the solution, without diminishing the supply of helium; thus any helium-containing impurity must be soluble in alcohol.

On the plate on which the helium line was strongest—the salt was KI—I could see a very faint line corresponding to an atomic weight 35 or thereabouts. I should have thought this was due to a trace of chloride among the potassium iodide, except for the fact that when KCl was substituted for KI this line was not strengthened. I have not yet been able to get this line strong enough to measure it with sufficient accuracy to decide whether the particle producing it has an atomic weight exactly equal to the difference of the atomic weights of potassium and helium.

The evolution of helium in exceptionally large amounts from the alkaline metals is interesting, since potassium, as Mr. Campbell has shown, is radioactive. I am disposed to regard the emission of helium from these metals as supporting the speculation I gave in a letter to 'Nature,' Feb. 13, 1913, that other elements besides radium, thorium, and the like, make attempts to expel α-particles (atoms of helium). In ordinary elements these particles have not enough energy to get away from the atom; they are, however, as it were, loosened, and can be detached by vigorous bombardment with cathode rays.

I now pass on to consider the effect of solution and subsequent evaporation on the evolution of X_3, which all the salts, including the calcium, ammonium, and silver ones, gave off in abundance. Solution and evaporation produced a marked diminution in the output of X_3 from Li_2CO_3, KI, KCl. It had little effect, however, on the output from LiCl, LiOH, KOH, $CaCl_2$. It will be noticed that these latter salts are very deliquescent, while those which are affected by solution are not. This suggests that the diminution in X_3, when it occurs, may be due to water being driven off when the salts are strongly heated after evaporation, the deliquescent salts recovering the water before bombardment, whilst the others do not. The X_3 will come out of the salt with cathode rays which are not fast enough to liberate helium.

These results show, I think, that the X_3 liberated from the dissolved salts was not simply absorbed by them, but was either manufactured from hydrogen in the presence of water, or liberated from the atoms of one or more of the elements in the salt, and that the presence of water is an important, it may be an essential, condition for its production by atomic disruption. If we suppose X_3 is made from hydrogen the function of the salt may be merely to supply the necessary water in a convenient form. X_3 is produced when the discharge from a Wehnelt cathode passes through gas at a low pressure, though in this case the bombardment of the walls of the tube by cathode rays is feeble; this and its sporadic appearance in discharge tubes would be accounted for if it were produced from water vapour.]

[*Note added July* 10, 1913.—I find that X_3 disappears when a mixture of it with hydrogen is sparked with sufficient oxygen to give a violent explosion.]

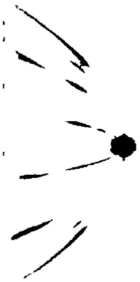

FIG. 2.

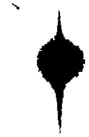

FIG. 3.

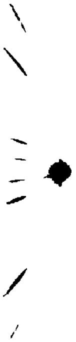

FIG. 7.

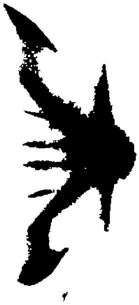

FIG. 10.

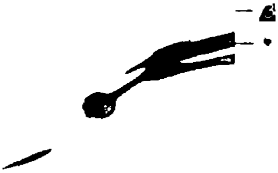

FIG. 11.

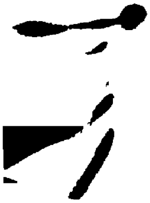

FIG. 13.

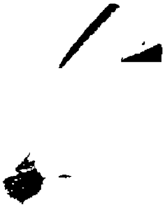

FIG. 13A.

FIG. 14.

FIG. 15.

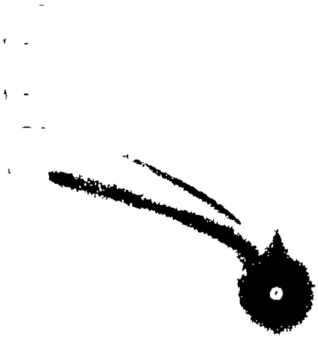

Fig. 12.

Fig. 16

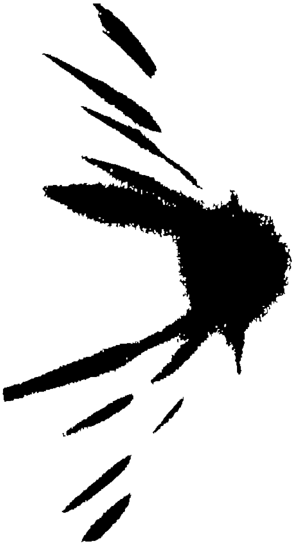

Fig. 17.

Fig. 18.

FIG. 19.

FIG. 20.

FIG. 22.

FIG. 23.

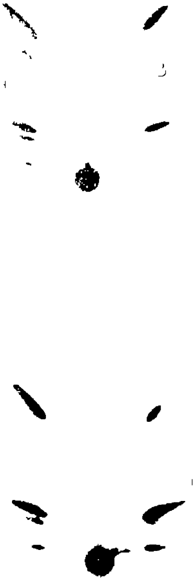

FIG. 24.

The Magnetic Materials in Claywares.

By Arthur Hopwood.

(Communicated by Prof. H. B. Dixon, F.R.S. Received May 14,—Read June 19, 1913.)

Robert Boyle* first observed the magnetic nature of burnt clays and found that a brick, after being heated in a fire and subsequently allowed to cool in the same position, became magnetised in the same direction as the earth's magnetic field. Later, J. B. Beccaria† observed that bricks or ferruginous stones which had been struck by lightning were also permanently magnetised in the same direction as the earth's magnetic field.

But Gheradi‡ was the first to make a systematic study of the magnetism of burnt clays. He examined all sorts of clay articles made at different epochs and at various places in Italy and Egypt, and demonstrated the existence of permanent magnetism in all kinds of earthenware or stoneware. Further, he observed that antique claywares permanently retained the magnetism induced in them during the process of baking, irrespective of the positions they afterwards occupied with respect to the earth's magnetic field. In brief, the researches of Gheradi established the existence of permanent magnetism in all kinds of antique and modern claywares, and also demonstrated its influence on the measurements of the terrestrial magnetic elements in brick edifices.

Taking advantage of the property which clay possesses of becoming magnetised during the process of baking and of permanently retaining the magnetism acquired through the action of the earth's magnetic field, Giuseppe Folgheraiter§ advanced the view that the various claywares found in excavations and ancient tombs afford an indelible record of the state of the earth's magnetism at the epoch and place of their manufacture, and thereby furnish us with an indirect means of enlarging our knowledge of the secular variation of the magnetic inclination of the earth. From various parts of Italy and Greece Dr. Folgheraiter collected a large number of antique vases and other clay articles, which had been placed in an upright position during the process of firing, and of which were also known the dates and places of their manufacture. He then determined the directions of the magnetic axes of these antique vases, which led him to assign definite values to the magnetic inclination at the time and place of their manufacture. Without entering into the numerous details of these indirectly interesting researches, it will be sufficient for our purpose to state briefly that the work begun by G. Folgheraiter, and more recently extended by B. Brunhes and P. David* and P. L. Mercanton,† had almost exclusively for its object the determination of the orientation of the magnetism in antique claywares as a means of extending the knowledge of the secular changes in the magnetic inclination of the earth.

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* 'Experimenta et Observationes Physicæ,' London, 1691, Chap. I, Expt. 12; 'The Philosophical Works of the Honourable Robert Boyle,' by Peter Shaw, 1st Edition, London, 1725, vol. 1, p. 504; 2nd Edition, London, 1738, vol. 1, p. 506; 'Works of the Honourable Robert Boyle,' by Thomas Birch, New Edition, London, 1772, vol. 5, p. 573.

† 'Observations et Mémoires sur la Physique,' par M. l'Abbé Rozier, Paris, 1777, vol. 9, pp. 382–384; vol. 10, pp. 14–16.

‡ 'Il Nuovo Cimento,' 1862, vol. 16, p. 384; 1863, vol. 18, p. 108; see further, Gage and Lawrence, 'Phys. Rev.,' 1899, No. 3, p. 304.

§ 'Roma, Reale Accad. Lincei Atti,' 1896, vol. 5, pp. 66–74, 127–135, 199–206, 242–249, 293–300; 1897, vol. 6, pp. 64–79; 1899, vol. 8, pp. 69–76, 121–129, 176–183, 269–275; see also 'Séances de la Société Française de Physique,' 1899, pp. 118–123.

In all these memoirs on the magnetism of burnt clays it is assumed that baked clays owe their magnetic properties entirely to the presence of magnetic oxide of iron, and that this is derived partly from the orientation of the magnetite originally present in the clays, and partly from the reduction of the ferric oxide of the clays during the process of burning. Numerous observations on different kinds of claywares led the author to conclude that this view was too limited, and it will be shown in the following pages that white, cream, grey, yellow, buff, red, or brown claywares are feebly or moderately magnetic owing to the presence of black unfused grains of unchanged magnetic minerals and bluish-black fused globules of ferruginous silicates; while flashed, brindled, or blue claywares are strongly magnetic owing to the presence of ferruginous silicates and magnetic oxide of iron.

Nature of the Magnetic Materials in Claywares.

White, cream, grey, yellow, buff, red, or brown claywares when carefully examined, preferably on a fractured surface, are found to be more or less speckled with black unfused grains or more frequently with bluish-black fused globules, varying in size from minute bubbles to large blisters. The unfused black grains are generally unchanged granules or concretions of either magnetic or non-magnetic ferruginous minerals originally present in the unbaked clays. The more common bluish-black fused globules are never present in the unburnt clays, and are always strongly attracted by a magnet.

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* 'Comptes Rendus,' 1901, vol. 133, pp. 155–157; 1903, vol. 137, pp. 975–977; 1904, vol. 138, pp. 41–42; 1905, vol. 141, pp. 567–568.

† 'Comptes Rendus,' 1906, vol. 143, pp. 139–140.

When heated to 1300° C. in the reducing atmosphere of a blue brick kiln, or to 1350° C. in the oxidising atmosphere of a china biscuit oven, the fused globules sometimes melt, but otherwise undergo no change. The analyses of the fused globules from different kinds of claywares show them to be complex ferruginous silicates of slightly variable composition. Hence white, cream, grey, yellow, buff, red, or brown claywares normally owe their magnetic properties, partly to the presence of black unfused grains of unchanged ferruginous minerals, and partly to the presence of bluish-black fused globules of complex ferruginous silicates.

Analyses of the Magnetic Globules in Claywares.

	Globules from salt-glazed sewer pipes (Burslem).	Globules from red bricks (Hanley).	Globules from blue bricks (Tunstall).
	per cent.	per cent.	per cent.
Silica	40·52	42·03	42·83
Alumina	17·85	16·50	15·50
Ferrous oxide (calc. from total iron)	30·73	31·65	34·27
Manganous oxide	0·92	0·74	0·83
Lime	4·33	4·55	2·74
Magnesia	4·82	3·53	2·93
Alkalies	0·58	0·90	0·72
	99·75	99·90	99·82

When grey, yellow, buff, red, or brown claywares have been flashed, *i.e.* partly reduced, in the baking process so that their surfaces become greenish-black or bluish-black in places, they invariably contain more fused globules of ferruginous silicates than the corresponding normally fired claywares, together with varying amounts of an unfused magnetic material present in the greenish-black or bluish-black patches. In some claywares, these unfused bluish-black patches can easily be separated mechanically from the fused globules of ferruginous silicates, but as their magnetic constituent is so uniformly distributed throughout the bluish-black patches it cannot be separated mechanically from the main body of the claywares. On analysis, a greenish-black patch on a piece of slightly flashed terra-cotta gave 2·1 per cent. of ferrous oxide and 6·5 per cent. of ferric oxide, indicating that only part of the ferric oxide had been reduced to magnetic oxide of iron, while a bluish-black patch on a badly-flashed red brick made from the same clay gave 2·8 per cent. of ferrous oxide and 5·7 per cent. of ferric oxide, corresponding to the proportions of these oxides in magnetic oxide of iron. Hence, the unfused magnetic material present in the greenish- or bluish-black patches on grey, yellow, buff, red, or brown claywares is magnetic oxide of iron.

Blue claywares made by strongly heating a highly ferruginous clay, first in an oxidising and finally in a reducing atmosphere, consist of a blue-black unfused interior speckled with bluish-black fused globules, and an external perfectly fused blue film. When a portion of a blue brick is heated to 1100° C. in the oxidising atmosphere of a red brick kiln, the external blue film and the internal bluish-black fused globules remain unaltered, while the blue-black unfused portion of the interior acquires the red colour of ferric oxide. Both the bluish-black fused globules and the blue-black unfused interior are strongly magnetic, and in some specimens they can be separated mechanically. On analysis, the fused globules in blue claywares are found to be ferruginous silicates somewhat similar in composition as well as properties to those present in white, cream, grey, yellow, buff, red, or brown claywares. On analysis, the unfused interiors of two strongly magnetic blue claywares gave 2·3 and 2·5 per cent. of ferrous oxide to 4·7 and 5·1 per cent. of ferric oxide respectively, corresponding to the proportions of these oxides in magnetic oxide of iron; while the unfused interiors of two less magnetic blue claywares made from the same clays gave 4·1 and 4·5 per cent. of ferrous oxide to 2·8 and 3·0 per cent. of ferric oxide respectively, showing that the reduction in the latter cases had proceeded beyond the limits requisite for the production of magnetic oxide of iron, and that ferrous oxide as well as ferroso-ferric oxide may be present in the unfused blue-black matrix of blue claywares. It follows from these analyses that flashed, brindled, or blue claywares always owe their strongly magnetic properties to the presence of complex ferruginous silicates and magnetic oxide of iron.

Origin of the Magnetic Materials in Claywares.

As ordinary clays contain but small amounts of magnetite only a small proportion of the magnetic oxide of iron present in flashed, brindled, or blue claywares can have been derived from the magnetite originally present in the clays, and consequently the larger proportion must obviously have been produced by the reducing action of the kiln gases on the finely divided oxides, hydroxides, or carbonates of iron distributed uniformly throughout the clays.

The derivation of the fused globules of ferruginous silicates is quite different from that of the magnetic oxide of iron. While the latter would appear to be derived generally from the precipitated or colloid oxides, hydroxides, or carbonates of iron disseminated throughout the clays, the former would appear to be derived from the granules or concretions of ferruginous minerals like iron pyrites, cupriferous pyrites, siderite, hæmatite, magnetite, menaccanite, chromite, glauconite, biotite, hornblende, etc., which always occur in clays in masses varying in size from minute particles to large pieces. It is well known by clayworkers* that when a clay containing granules or concretions of ferruginous minerals is easy-fired in a strongly oxidising atmosphere, these minerals are left in the product as unfused black grains, while if the clay be fast-fired or hard-fired in a slightly oxidising or neutral atmosphere, or better if the clay be over-fired in a slightly reducing atmosphere, these minerals fuse with the surrounding matrix, producing small bubbles or large blisters of a bluish-black ferruginous slag. In conformity with this, the author observes that easy-fired white, cream, grey, yellow, buff, red, or brown claywares are less magnetic than hard-fired claywares and considerably less magnetic than over-fired claywares made from the same clays.

To test these explanations of the origin of the magnetic materials present in claywares, six clays used in the manufacture of different kinds of claywares were heated separately in different kilns ranging in temperature from 600° to 1350° C. The clays selected for investigation were a china clay, a ball clay, a stoneware clay, a fireclay, a common brick clay, and a red terra-cotta clay, which contained 0·27, 0·55, 1·3, 2·2, 3·5, and 5·5 per cent. of iron respectively. The granular and concretionary ferruginous minerals were removed from portions of these clays by passing them through a fine sieve and subjecting them to an electromagnet, then elutriating the powders with water in a Schöne's apparatus,† and finally collecting the purified clays from the suspension in water by sedimentation. The purified and the naturally occurring clays were then pressed separately into small tiles and heated whilst enclosed in seggars in the most strongly oxidising portions of (1) a ceramic thermoscope kiln raised to 600° C. in 12 hours; (2) a white earthenware enamel kiln raised to 750° C. in 10 hours; (3) a white earthenware majolica kiln raised to 1000° C. in 20 hours; (4) a red terra-cotta kiln raised to 1100° C. in 80 hours; (5) a reddish-brown roofing tile kiln raised to 1180° C. in 80 hours; (6) a white earthenware biscuit oven raised to 1250° C. in 40 hours; and (7) a china biscuit oven raised to 1350° C. in 40 hours. In every case, the purified clays gave white, cream, grey, buff, red, or brown non-magnetic bodies free from black specks of either unfused grains or fused globules, showing that the magnetisation of ordinary clays, when heated in strongly oxidising kilns, originates in the granular or concretionary ferruginous minerals and not in the precipitated or colloid oxides, hydroxides, or carbonates of iron present in the clays. The naturally occurring clays heated to 600°, 750°, or 1000° C. in strongly oxidising atmospheres gave white, cream, grey, buff, or red magnetic bodies, which were speckled with black unfused grains of unchanged ferruginous minerals, but with no bluish-black fused globules of ferruginous silicates; moreover, the amounts of magnetic materials they contained were rather less than those present in the unbaked clays, showing that ordinary clays, when heated in strongly oxidising kilns ranging in temperature from 600° to 1000° C., become magnetised only by the orientation of the magnetic minerals originally present in the unburnt clays. The naturally occurring clays, when heated to 1100° C. in the oxidising part of the red terra-cotta kiln, left white, cream, grey, buff, or red magnetic bodies speckled with many black unfused grains of unchanged ferruginous minerals and a few bluish-black fused globules of ferruginous silicates; further, when the same clays were heated in the oxidising portions of the previously mentioned, higher temperature, clayware kilns they left similarly coloured magnetic bodies generally containing more fused globules of ferruginous silicates and less unfused grains of unchanged ferruginous minerals, showing that ordinary clays, when heated in oxidising clayware kilns ranging in temperature from 1000° to 1350° C., become magnetic, partly owing to the orientation of unchanged magnetic minerals and partly to the conversion of granular or concretionary ferruginous minerals to fused globules of complex ferruginous silicates.* When the clays were heated in the slightly reducing portions of the above clayware kilns, or better when heated to 1300° C. in the strongly reducing atmosphere of a blue brick kiln, the purified clays yielded white, grey, or blue magnetic bodies containing unfused magnetic oxide of iron but free from fused globules of ferruginous silicates, while the naturally occurring clays yielded similarly coloured magnetic bodies containing unfused magnetic oxide of iron and also fused globules of ferruginous silicates. This shows that ordinary clays when heated strongly in reducing kilns become highly magnetic due to the formation of complex ferruginous silicates and magnetic oxide of iron.

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* *Cf.* E. Orton, 'Trans. Amer. Cer. Soc.,' 1903, vol. 5, pp. 377–430.

† *Cf.* 'Zeitschr. f. Anal. Chem.,' vol. 7, p. 20.

Amounts of the Magnetic Materials in Claywares.

In view of the fact that the magnetic disturbances existing in magnetic observatories and physical laboratories have in many cases been found to be due to the brickwork of the buildings,† magneticians and physicists have to be very careful in the selection of building materials to be employed for such purposes.* In consequence, the author has determined the combined amounts of the magnetic materials present in the different kinds of claywares made in various parts of the country, in order to ascertain which would and which would not be suitable for the construction of such buildings.

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* *Cf.* G. Folgheraiter, 'Roma, Reale Accad. Lincei Atti,' 1895, vol. 4, 2, pp. 78–85; 1897, vol. 6, 2, pp. 368–376.

† *Cf.* Lamont, 'Abhandl. d. K. Bayr. Akad. d. Wiss., Math. Phys.,' 1847, vol. 5, p. 24; F. Kohlrausch, 'Wied. Ann.,' 1883, vol. 19, p. 142; R. W. Willson, 'Amer. Journ. Sci.,' 1890, vol. 39, pp. 87–93, 456–470.

The combined amounts of the magnetic materials present in each kind of clayware were determined by powdering separately several specimens, representing all grades from the best to the worst of each kind, and then weighing the black particles which adhered to a 12-inch horse-shoe magnet when its poles were moved repeatedly through the finely powdered mass placed upon a piece of glazed paper. In the case of white, cream, grey, yellow, buff, red, or brown claywares, the complete separation of the black magnetic materials from the non-magnetic matrix was usually accomplished after subjecting their powders to the magnet for 5–10 hours, but in the case of flashed, brindled, blue, or black claywares the complete separation of the magnetic from the non-magnetic materials could not always be made even by a much more prolonged application of this process.

For convenience of description the claywares are roughly divided according to their colour into six classes, *i.e.* white, grey, yellow, red, blue, or black claywares. Each of these classes contains widely different varieties, which are distinguished in this paper by brief statements of their uses or the clays and other materials employed in their production at the same time as the variation of the combined amounts of the magnetic materials in each variety is given.

(i) *White Claywares.*—Porcelain or china made either from a mixture of china clay and felspar, or from a mixture of china clay, ball clay, cornish stone, and calcined bones, is always feebly magnetic,† and contains from traces to 0·002 per cent. of black magnetic materials. Glazed white earthenware or glazed white stoneware made for ornamental, household, or electrical purposes, from a mixture of china clay, ball clay, cornish stone or felspar, and flint, is also feebly magnetic, and contains from 0·0005 to 0·005 per cent. of black magnetic materials. The coarser white or cream terra-cotta and also ornamental or facing bricks made from common ball clays are more magnetic, and generally contain from 0·001 to 0·1 per cent. of magnetic materials; while the still coarser white or grey firebricks made from china clay refuse or from disintegrated granite usually contain from 0·01 to 1·0 per cent. of black magnetic substances, although as much as 5 per cent.

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* *Cf.* C. C. Marsh, 'Observations at the United States Naval Observatory,' Washington, 1887, Appendix I, pp. 1–37.

† *Cf.* M. Faraday, 'Phil. Trans.,' 1846, vol. 53, Part I, p. 29.

is frequently found in badly-fired specimens having speckled bodies or flashed surfaces. Further, the white, pink, green, or blue floor tiles for tesselated or mosaic pavements made by colouring white-burning clayey mixtures with a zinc, tin, nickel, chromium, or cobalt stain are technically and magnetically similar to the finer qualities of white earthenware, and contain from 0·0005 to 0·005 per cent. of black magnetic bodies.

(ii) *Grey Claywares.*—Glazed stoneware made from siliceous ball clays for culinary, preserving, bottling, or electrical purposes usually contains from 0·001 to 0·5 per cent. of magnetic materials, although more than 1 per cent. is often present in badly speckled or flashed bodies. The coarser salt-glazed stoneware made from vitreous fireclays for sanitary purposes is generally more magnetic and usually contains from 0·015 to 5·0 per cent. of black magnetic materials, but in badly speckled, black-cored, or flashed specimens the proportion is often as high as 10 per cent.

(iii) *Buff or Yellow Claywares.*—Cream or buff claywares made from various grades of tertiary or carboniferous buff-burning fireclays vary considerably in their magnetic qualities. Glazed buff tiles, teapots, and similar goods made for ornamental or household uses usually contain from 0·001 to 0·5 per cent. of magnetic materials, though those with badly speckled or flashed bodies, almost invariably covered with dark-coloured glazes, often contain more than 1 per cent. Buff floor tiles made from high grade buff-burning clays for tesselated or mosaic pavements are always feebly magnetic, and usually contain from 0·001 to 0·25 per cent. of black magnetic materials; but the ordinary buff quarry floor tiles, terra-cotta, and also paving, facing, or ornamental bricks generally contain from 0·005 to 1·0 per cent. of magnetic substances. The coarser buff fire-bricks, glazed bricks, and similar refractory wares made from lower grade fireclays are more magnetic, and generally contain from 0·01 to 5·0 per cent. of black magnetic substances, while 10 per cent. is often found in specimens having black cores, speckled bodies, or flashed surfaces. Similarly, the cream or yellow claywares made from calcareous ferruginous clays or calcareous clayey mixtures vary somewhat like the refractory claywares in their magnetic properties, and usually contain from 0·005 to 5·0 per cent. of black magnetic substances. Further, the grey or drab floor tiles for tesselated or mosaic pavements made from a high grade buff-burning clay and manganese dioxide or puddler's tap cinder, are invariably more magnetic than the technically similar buff floor tiles, and usually contain from 0·005 to 1·0 per cent. of black magnetic materials.

(iv) *Red or Brown Claywares.*—Red or brown claywares made from highly ferruginous clays vary greatly in their magnetic properties. Glazed red tiles, teapots, and similar wares made for ornamental or household purposes generally contain from 0·001 to 1·0 per cent. of magnetic materials, though as much as 5 per cent. is often found in specimens having badly speckled or flashed bodies covered with dark-coloured glazes. Salmon or red floor tiles made from high grade red-burning clays or clayey mixtures for tesselated or mosaic pavements, are always feebly magnetic, and contain from 0·001 to 0·3 per cent. of black magnetic materials; but the ordinary red quarry floor tiles, plant pots, terra-cotta, and also ornamental, paving, or facing bricks, generally contain from 0·005 to 1·0 per cent. of black magnetic substances. The coarser common red building bricks and red fire-bricks, as well as red and brown roofing tiles, are more magnetic and generally contain from 0·01 to 10 per cent. of black magnetic substances, but 20 per cent. is frequently found in badly fired specimens having black cores, speckled bodies, or flashed surfaces. Further, the chocolate floor tiles for tesselated or mosaic pavements made from a high grade red-burning clay and manganese dioxide or puddler's tap cinder, are invariably more magnetic than the technically similar red floor tiles, and usually contain from 0·005 to 1·0 per cent. of black magnetic bodies.

(v) *Blue or Brindled Claywares.*—Blue, brindled, or flashed claywares made by heating ferruginous clays first in an oxidising, and finally in a reducing atmosphere, are always very magnetic, the intensity of their magnetisation depending upon the extent of the conversion of the finally disseminated oxides of iron and the grains of ferruginous minerals to magnetic oxide of iron and ferruginous silicates. Brindled bricks and other partially reduced claywares like grey, buff, or red claywares having flashed surfaces, yield powders of which 10 to 50 per cent. usually adheres to a magnet, while blue bricks, blue quarry floor tiles, and other completely reduced claywares give impalpable powders, the whole of which often adheres to a magnet. This shows that either the whole mass of a uniformly blue clayware is a ferruginous silicate having strongly magnetic properties,* or more probably that the magnetic oxide of iron produced by the reduction of the homogeneously distributed ferric oxide is uniformly disseminated throughout the mass of the clayware, making the separation of the magnetic from the non-magnetic materials impossible by mechanical means.

(vi) *Black Claywares.*—The greatest variation in magnetic qualities is found in the black claywares used for ornamental or paving purposes. Those made from a ferruginous clay, manganese dioxide, and ironstone, are usually feebly magnetic and generally contain from 0·01 to 1·0 per cent. of magnetic materials; but those made from a ferruginous clay and

* *Cf.* E. Orton, 'Trans. Amer. Cer. Soc.,' 1903, vol. 5, pp. 377–430.

puddler's tap cinder are generally strongly magnetic, and usually yield powders the whole of which adheres to the poles of a magnet.

The general conclusions to be drawn from these analyses are that all baked claywares are magnetic, and that different kinds, as well as different specimens of the same kind, contain extremely varying amounts of black magnetic materials. Black, blue, or brindled claywares, and also badly-fired grey, yellow, buff, red, or brown claywares having black interiors, speckled bodies, or flashed surfaces, are almost invariably strongly magnetic; while white, cream, grey, yellow, buff, red, or brown claywares having none of these imperfections are always feebly magnetic. Whenever claywares have speckled bodies, flashed surfaces, or black cores, they are always much more magnetic than the corresponding ones free or relatively free from these defects; and, consequently, the intensities of the magnetisation of any white, cream, grey, yellow, buff, red, or brown claywares can be roughly inferred from a cursory examination of the extent of the specking, flashing, or black-coring they exhibit.

Building Materials for Physical Laboratories and Magnetic Observatories.

The strongly magnetic nature of certain claywares shows that great care must be exercised in the choice of these materials for the construction of magnetic observatories and physical laboratories, or serious disturbances may take place during observations with delicate magnetic instruments.

The suitability of claywares for building purposes, or the choice between two or more claywares, can often be readily inferred from a cursory examination of their outward characteristics. In other cases, the problem can be solved very readily by determining the combined amounts of the magnetic materials in their powders by extraction with a magnet.

Many physical laboratories are in existence in which greater care in the selection of the claywares used would have considerably reduced the magnetic disturbances existing in them. Some are built with badly speckled and flashed bricks, and others even contain brindled and blue claywares. These are not by any means the least magnetic of the claywares, and consequently on delicate magnetic instruments they will cause disturbances which could have been easily reduced to a negligible extent by a more careful selection of the building materials.

On the Force Exerted on a Magnetic Particle by a Varying Electric Field.

By J. G. Leathem, M.A., D.Sc., Fellow of St. John's College, Cambridge.

(Communicated by Sir J. Larmor, F.R.S. Received May 21,—
Read June 26, 1913.)

With a view to explaining magnetism as a purely electrical phenomenon it is customary in the modern theory of electromagnetism to define magnetic force as a solenoidal vector whose curl is 4π times the electric current, and the magnetisation of a material element as half the angular moment of the motion of electricity in the element.* But it is clear that the definitions remain unjustified until it has been shown that the relations of these quantities to one another and to the other quantities of the theoretical formulation are the same as the relations which experience indicates as subsisting between the corresponding physical quantities.

It is, therefore, an essential part of the test of the theory to ascertain the theoretical value of the force exerted by a varying external field upon a magnetic particle.

The particle is supposed to contain electric charge, whether continuously or discretely distributed it is not necessary at the moment to specify. This charge is supposed to be in motion relative to the particle, and the force exerted on the particle by the electromagnetic field is simply the resultant of the forces which the field exerts on the electric charge.

Let w denote the velocity of an origin O situated in the particle and moving with it, and let an element of electric charge de belonging to the particle have co-ordinates x, y, z referred to non-rotating axes with O as origin. Then the velocity of de has components $w_x+\dot{x}$, $w_y+\dot{y}$, $w_z+\dot{z}$, and may be denoted by $w+u$.

The external field is specified by the magnetic intensity $\mathrm{H}, (\alpha, \beta, \gamma)$, and the æthereal displacement $\mathrm{D}, (f, g, h)$. If these letters without suffix denote the values at O, the value at (x, y, z) is derived by means of the operator of Taylor's expansion, namely

$$\exp\left(x\frac{\partial}{\partial x}+y\frac{\partial}{\partial y}+z\frac{\partial}{\partial z}\right).$$

In terms of the electromagnetic system of units the force on an element of charge is

$$\{4\pi c^2\mathrm{D}+[w+u, \mathrm{H}]\}\, de,$$

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* *Cf.* H. A. Lorentz, 'Encyk. der Math. Wiss.,' vol. v, 2, p. 181; and Larmor, 'Æther and Matter,' § 64.

where C is the velocity of light, and the square bracket denotes the vector-product. Consequently the resultant force on the particle is

$$\mathrm{F}=\int\left\{\exp\left(x\frac{\partial}{\partial x}+y\frac{\partial}{\partial y}+z\frac{\partial}{\partial z}\right)\right\}\{4\pi\mathrm{C}^2\mathrm{D}+[w+u,\,\mathrm{H}]\}\,de,$$

the integral being extended to all the charges in the particle. Here the exponential operator applies only to the components of D and H; it will, of course, be expanded, and all but the earlier terms will be considered negligible.

The following notation is convenient:—

$$\int de=e,\qquad \int(x,y,z)\,de=(p_x,p_y,p_z),$$

$$\int(x^2,y^2,z^2,yz,zx,xy)\,de=(q_{11},q_{22},q_{33},q_{23},q_{31},q_{12}).$$

Here e is the algebraic total charge of the particle, p_x, p_y, p_z are the components of its electric polarisation, while the q's are analogous to moments and products of inertia and may be called the 'second electric moments' of the particle.

If we assume that the second moments are so small as to be negligible we get

$$\mathrm{F}_x=\left(e+p_x\frac{\partial}{\partial x}+p_y\frac{\partial}{\partial y}+p_z\frac{\partial}{\partial z}\right)(4\pi\mathrm{C}^2f+w_y\gamma-w_z\beta)$$
$$+\int\left(1+x\frac{\partial}{\partial x}+y\frac{\partial}{\partial y}+z\frac{\partial}{\partial z}\right)(\dot y\gamma-\dot z\beta)\,de.$$

Now the components of magnetisation m_x, m_y, m_z, are defined by the relations

$$\int(y\dot z-z\dot y,\quad z\dot x-x\dot z,\quad x\dot y-y\dot x)\,de=2\,(m_x,m_y,m_z);$$

and we note further that

$$2\int(x\dot x,y\dot y,z\dot z)\,de=\frac{d}{dt}(q_{11},q_{22},q_{33}),$$

$$\int(y\dot z+z\dot y,\quad z\dot x+x\dot z,\quad x\dot y+y\dot x)\,de=\frac{d}{dt}(q_{23},q_{31},q_{12});$$

hence $\int y\dot z\,de=\tfrac12\dot q_{23}+m_x,\qquad \int z\dot y=\tfrac12\dot q_{23}-m_x,$

with other similar equalities. Accordingly

$$\mathrm{F}_x=\left(e+p_x\frac{\partial}{\partial x}+p_y\frac{\partial}{\partial y}+p_z\frac{\partial}{\partial z}\right)(4\pi\mathrm{C}^2f+w_y\gamma-w_z\beta)$$
$$+m_y\frac{\partial\beta}{\partial x}+m_z\frac{\partial\gamma}{\partial x}-m_x\left(\frac{\partial\beta}{\partial y}+\frac{\partial\gamma}{\partial z}\right)$$
$$+\text{ terms involving time-fluxes of the } q\text{'s}.$$

This formula is general. With a view to considering a purely magnetic particle we may suppose that the total charge e is zero, and that there is no electric polarisation, so that the first term of F_x is zero.

Let us further suppose that there is such permanence in the configuration or average configuration of electric charge in the particle that there is a set of axes (possibly rotating, provided the rotation be not extremely rapid), with O as origin, with respect to which the second electric moments are constant, or have constant average values. When this holds good the time-fluxes of the q's are either zero or (for rotating axes) small of the same order of smallness as the q's themselves, and so may be neglected.

Thus, for a purely magnetic particle,

$$\begin{aligned} F_x &= m_y\frac{\partial\beta}{\partial x}+m_z\frac{\partial\gamma}{\partial x}-m_x\left(\frac{\partial\beta}{\partial y}+\frac{\partial\gamma}{\partial z}\right), \\ &= m_x\frac{\partial\alpha}{\partial x}+m_y\frac{\partial\beta}{\partial x}+m_z\frac{\partial\gamma}{\partial x}, \\ &= \left(m_x\frac{\partial}{\partial x}+m_y\frac{\partial}{\partial y}+m_z\frac{z}{\partial z}\right)\alpha+m_y\left(\frac{\partial\beta}{\partial x}-\frac{\partial\alpha}{\partial y}\right)-m_z\left(\frac{\partial\alpha}{\partial z}-\frac{\partial\gamma}{\partial x}\right); \end{aligned}$$

or, vectorially,

$$\begin{aligned} F &= \left(m_x\frac{\partial}{\partial x}+m_y\frac{\partial}{\partial y}+m_z\frac{\partial}{\partial z}\right)H+[m,\ \text{curl } H], \\ &= \left(m_x\frac{\partial}{\partial x}+m_y\frac{\partial}{\partial y}+m_z\frac{\partial}{\partial z}\right)H+4\pi[m,\ \dot{D}]. \end{aligned}$$

The first term of F is the ordinary formula for the force exerted on a magnetic particle, regarded as a polarised combination of positive and negative magnetism, by a field of magnetic force. The second term is rather unexpected; it represents a mechanical force exerted on a magnet by a current of æthereal displacement, perpendicular to the current and to the magnetic moment, and proportional to the product of the two and the sine of the angle between them. If experimental evidence were definitely against the existence of such a force the theory would be at fault.

It might seem possible to test the matter by hanging a small magnet horizontally between the horizontal plates of a charged condenser and then effecting a non-oscillatory discharge of the condenser. If the upper plate were originally charged with positive electricity, the displacement current on discharge would be upwards, and an eastward impulse on the magnet might be looked for. But when it is remembered that the formula is in terms of electromagnetic units it will be seen that the charge on the condenser required to impart sensible motion to the magnet would probably be enormously great. Thus an experimental test may well be out of the question.*

With regard to the hypothesis of the exact or average constancy of the values of the second electric moments of a magnetic particle, it is to be remarked that exact permanence of configuration in a whirling distribution of electricity is to be looked for only when the rotation is entirely about one axis round which the distribution is circularly symmetrical. This does not seem to be a probable state of affairs in a magnetic particle. On the other hand an average permanence of configuration may be claimed to exist for quite a complicated system of orbital motions of separate electrons provided the geometrical configuration of the orbits be permanent. All that is required for permanence of the average electric configuration is that the time-average be taken for an interval of time which is great compared with all the periods that the various electrons take to describe their respective orbits, or, if one orbit be described by several electrons, the interval between successive recurrences of the same electric configuration in that orbit. If the velocities in the orbits are very great only a very minute interval of time need be taken in order to get constant time-averages. In the case of a magnetic particle possessing as a whole a rotatory motion of not very great rapidity the permanence of the time-averages of the second moments would be with respect to moving axes.

It is indeed conceivable that the duration of any obtainable displacement current might be too short to permit the substitution of time-averages for a more accurate tracing of the changes in the configuration of charge in a single particle; in the case, however, of a magnet made up of a large number of particles any resultant effect would correspond to an average for all the particles, in which average the fortuitous character of the instantaneous circumstances for a single particle would be obliterated by force of numbers and the probably quite irregular distribution of phase.

Sir Joseph Larmor, to whom the writer is indebted for suggestions and criticisms, suggests as interesting the following aspect of the supplementary term in the above hypothetical expression for the force on a magnetic particle:—

If a magnet were merely a whirling distribution of electricity then the forces acting on a region of it ought, like those on any other distribution of electricity, to be expressible as the result of a quasi-stress over the boundary and a quasi-momentum in the region. But the commonly assumed forces on a medium of magnetic quality are not so expressible;[*] consequently the force on a whirl of electricity is not completely expressed by the usual formula of magnetic type in terms of its equivalent magnetic moment. The addition of the above obtained subsidiary term of much smaller order is just what is needed to restore the possibility of a stress-momentum specification. The term being too small for any light to be thrown upon its existence by direct experiment, there is no reason for excluding it; if we postulate the universality of the stress-momentum representation we must retain it.

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* Another possible difficulty is that the displacement current might alter the state of magnetisation, so that *m* would be a function of D and D. In so far as this held good the result would be uncertain.

For the sake of completeness it may be mentioned that, to the degree of approximation above contemplated, the torque on a particle is

$$[p, \{4\pi c^2 D + [w, H]\}] + [m, H] + \text{terms involving time-fluxes of the second electric moments.}$$

The part of this applicable to a purely magnetic particle is the same as is got from ordinary magnetic theory.

It is to be noted that the expressions here discussed refer only to the action of an external field on a particle. They do not include the action upon an electron of its own field or of the field due to other electrons belonging to the same particle. Thus radiation and electromagnetic inertia do not enter into the discussion.

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[*] Larmor, "Dynamical Theory, etc.," 'Phil. Trans.,' A, 1897, vol. 190, § 39.

On the Luminosity Curve of a Colour-blind Observer.

By W. WATSON, D.Sc., F.R.S., with an Appendix by Dr. F. W. EDRIDGE-GREEN.

(Received May 24,—Read June 26, 1913.)

In a recent paper communicated to the Society, the author gave the results of a long series of measurements which indicate that the luminosity curves of colour-blind persons can be deduced from the curve obtained by a person who has normal colour vision, by making the necessary allowance for their colour defect. In the discussion on this paper, Dr. Edridge-Green mentioned that he had made measurements by a flicker method of the luminosity for a colour-blind observer, and that he had found it to agree exactly with the normal.* This result being entirely opposed to the results obtained by the author, it seemed of great interest to investigate the matter further. This, owing to the kindness of Dr. Edridge-Green and the gentleman (Mr. C.), has been possible, as luminosity curves for Mr. C. and Dr. Edridge-Green have been obtained with the author's apparatus, and in this note are given the results.

The measurements obtained in the bright part of the spectrum, extending from the red to the bluish-green, are given in the following table:—

Wave-length of coloured light. Å.U.	Luminosity.		Difference.	Luminosity calculated for 0·4 G.S.
	Mr. C.	Dr. Edridge-Green.		
6090	84·0	75·3	+8·6	84·8
5890	101·0	94·0	+7·2	99·6
5800	100·0	99·2	+0·8	100·0
5560	82·6	91·8	−9·2	86·5
5410	67·3	74·6	−7·3	67·0
5270	49·9	58·0	−8·1	49·2
5140	35·4	42·3	−7·0	33·7

The numbers obtained by Dr. Edridge-Green are in good agreement with those of the majority of persons having normal colour vision. The only difference in his case is that his numbers in the blue and violet are somewhat higher than the normal. This, as shown in the previous paper, is probably due to the macular pigmentation being rather less than the normal, which also accounts for his luminosity at wave-length 5800 Å.U. being a little low.

Mr. C.'s luminosity, on the other hand, is decidedly different from the normal, the luminosity being high on the red side of 5800 and low on the blue side of this point. This is what one would expect if Mr. C. is partly green-blind, and in the last column of the table are given the values of the luminosity of a person who has only 0·4 of the normal green sensation obtained by the method described in the afore-mentioned paper. It will be observed that these calculated values agree very fairly with Mr. C.'s observed numbers; in only one case, namely, at 5560 Å.U., is the difference at all marked. This difference is probably entirely due to errors of observation, Mr. C. never having used the apparatus before and only one series of measurements being taken.

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* Dr. Edridge-Green has been good enough to supply the particulars of the results he has obtained, and these are given in Appendix I.

It thus appears that Mr. C. is not an exception and that his case really supports the results given in the previous paper. When Dr. Edridge-Green examined him red and green lights were compared, these lights being obtained by means of coloured glasses. No doubt in this way a fairly pure red was obtained. The green, on the other hand, would contain a considerable proportion of blue light. It is quite possible that this blue light affected the results, as in the case of most observers the results obtained with blue or violet light by the flicker method are very variable and depend enormously on the brightness of the light employed. Further, the experimental error when a red is compared directly with a green, as in Dr. Edridge-Green's measurements, is very much greater than when either is compared with a white. Further it is to be remembered that in the case of persons having a deficiency in the green sensation the effect produced on the luminosity can only be small, as is shown in the curves given in the previous paper. Hence I think it quite possible that Dr. Edridge-Green's apparatus may not have been sufficiently sensitive to detect the difference between Mr. C.'s luminosity and the normal, particularly when, owing to the mixture of blue with the green, the effect to be observed was probably partly masked by this blue.

APPENDIX I.—*Results of the Examination of Mr. C. by Dr. Edridge-Green.*

Colour Perception Spectrometer.—Light, petroleum, 180 metre-candles. Eye light-adapted.

Saw two colours in brilliant spectrum, yellow and blue with grey interval between. Red appeared as a darker yellow. Neutral area, 5013–5040. Area of greatest luminosity, 5655–6319.

Monochromatic regions.	**Designation of region by him.**
754 –521·5	Yellow.
521·5–508	Green or grey.
508 –501·3	Green or grey.
501·3–492	Blue-green.
492 –483	Green-blue.
483 –417	Blue.

Saw small area of light 549–561 to same point of extinction as I did.

Lantern Test.—Tested with large aperture, ⅞ inch in diameter, from a distance of 20 feet. Called neutral, green; red, yellow and green; green, yellow, orange and red; and yellow, red and green. Recognised small points of coloured light on convex mirror from the same distance as I did, but could not tell their colours.

Bead Test.—Put red, orange, pink and brown in red division; orange, pink, and white in yellow division; green, coral, pink, brown and grey in green division; and blue and purple in blue division.

Rayleigh Equation (0 being full red, 25 full green).—Made a match at 17·7 and 18. Said my match 15 was not correct, the mixed colour appearing to him darker and greener.

A Comparison of Red and Green by Flicker Method.—The luminosities of a red and a green glass were compared with the Simmance-Abady photometer. The red glass transmitted rays 780–627 and feebly from 627 to 617. The green transmitted rays very imperfectly 605–575 and better the remainder of the spectrum 575–424. The filament of an osram incandescent light cannot be seen through both glasses combined. His ratio was 4·1 R/G for two consecutive observations, my ratio was 4·1 R/G.

Phosphorescence of Mercury Vapour after Removal of the Exciting Light.

By F. S. Phillips.

(Communicated by the Hon. R. J. Strutt, F.R.S. Received June 10,—
Read June 26, 1913.)

[Plate 4.]

§ 1. *Introduction.*

By means of Becquerel's phosphoroscope the fluorescence of solids has been shown to be persistent, but up to the present phosphorescence in the case of liquids and gases has not been observed. That of solids has generally been explained as due to chemical reactions brought about by impurities, while in the case of gases it has been considered that damped vibrations of the rapidity of those connected with light could not be conceived as persisting for a sufficiently long time for the necessary observations to be made. On the other hand, because of their relative simplicity, gases and vapours have been recognised as being eminently suitable for the study of fluorescence and kindred phenomena. Wood has applied the phosphoroscope to the case of sodium vapour, with however a negative result.

In the present experiment I have attacked the problem in a different way. The method used was to pass a beam of the exciting light transversely across a rapidly moving column of mercury vapour, obtained by distillation *in vacuo.* Then if the fluorescence of the vapour persists the luminosity should be carried along with the stream. The fluorescence was excited by 2536 light which was obtained by means of a quartz mercury lamp. Under suitable conditions the vapour could be seen to be still fluorescing, after it had passed a distance of some 18 inches from the point of excitation.

The fluorescence of mercury vapour was first observed by Hartley,[*] it has been further investigated by Wood.[†] The latter obtained the spectrum of the fluorescence excited by the light derived from the cadmium spark, and found that it was mainly continuous, but that under certain conditions the 2536 mercury line made its appearance. Wood has shown in a later paper[‡] that 2536 light produces resonant radiation even when the mercury vapour has only the very small density corresponding to ordinary temperatures. Under these circumstances the exciting radiation could penetrate a distance of a few centimetres into the vapour, without total absorption taking place, but if the temperature was higher and the vapour consequently denser, the radiation could only penetrate a few millimetres.

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[*] 'Roy. Soc. Proc.,' 1905, vol. 76, p. 428.

[†] 'Phil. Mag.,' August, 1909.

[‡] 'Phil. Mag.,' May, 1912.

§ 2. *Preliminary Experiments.*

Wood does not appear to have stated that this 2536 light produces visible fluorescence in mercury vapour. This, however, is the case and it is excited at a much lower pressure than when cadmium light is used. This latter fact is of great importance, in making possible the present method of showing the phosphorescence.

The fluorescence may be easily shown in a small exhausted quartz bulb containing a globule of mercury. If the bulb is uniformly heated to some 350° C., and then while cooling a concentrated beam of 2536 light is passed through it, the following interesting changes take place. At the highest temperature the vapour does not show any appreciable fluorescence, but as the bulb cools, the track of the beam gradually becomes illuminated with a bluish-green light. The fluorescence may conveniently be divided into two parts, that along the main track of the beam and the portion that extends for about 1 mm. from the place where the beam enters the bulb. At an early stage in the cooling the former reaches its maximum, and then begins to decrease in intensity. But the spot of fluorescence at the commencement of the beam does not begin to decrease in brightness until all the rest has disappeared. It then gradually fades away, and before the bulb reaches the temperature of the room all fluorescence has disappeared.

There are apparently three distinct phenomena excited by 2536 light in mercury vapour:—

(1) Resonant radiation, that exists over a long range of pressure from about one thousandth part of a millimetre to about 1 cm.

(2) Ordinary fluorescence, which does not rapidly grow less bright as the beam passes through the vapour; this exists when the pressure of the mercury vapour is about 1 cm.; and

(3) Local fluorescence at the point of entrance of the beam, that exists at much lower pressures than the ordinary fluorescence, but not at the very low pressure corresponding to ordinary temperature. It is this local fluorescence that has been found to be persistent.

A roughly made quartz monochromator was used in conjunction with the mercury lamp, and in order to obtain as much light as possible the slit of the monochromator was arranged so that it was horizontal and parallel to the luminous tube of the lamp. A Westinghouse Cooper-Hewitt lamp made of fused quartz was used in these experiments. Wood had previously found that when such a lamp became hot it lost its efficiency for producing resonant radiation in about five seconds after starting. The heating up of the lamp similarly affected the excitation of the persistent fluorescence, but in this case the falling off of intensity was not as rapid as that of the resonant radiation, yet after the lapse of one minute the effect was many times less powerful than at first. This trouble was entirely overcome by water-cooling the lamp, both the resonant radiation and the fluorescence being as good after an hour's run as when the lamp was first lit.

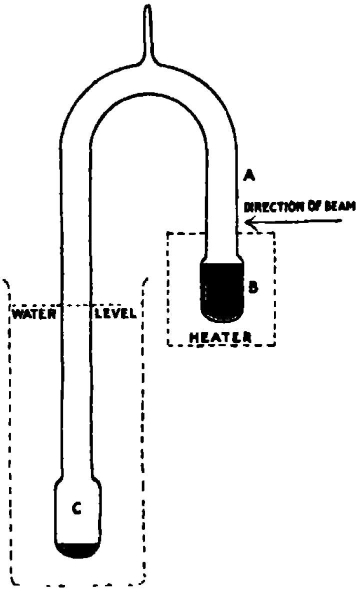
The reason for the hot lamp being less effective than the cold one has been pointed out by Wood. It is illustrated in fig. 1, Plate 4. This shows the spectra of the lamp when hot and when cold. The 2536 line in the hot lamp is unsymmetrically broadened and shows a magnificent reversal, while the same line in the cold lamp can be obtained as sharp as desired even in the sixth order of a Rowland grating. The upper spectrum shows the 2536 line as produced by the cooled lamp, while the lower one was obtained with the lamp hot, as it is ordinarily used. The symmetrical lines in this latter spectrum are ghosts.

Both the resonant radiation and the persistent fluorescence were excited by no mercury lines other than the 2536 line. Since the resonant radiation disappears as soon as the line broadens and becomes reversed, Wood inferred that it is only stimulated by radiations within very narrow limits of wave-length. The limits of wave-length that excite the persistent fluorescence are also very narrow, although possibly not quite so restricted as those that produce resonant radiation. There seems to be some connection between the two effects.

The cooling of the lamp was brought about by allowing water to run freely over both poles, while the tube between had a water-jacket half way round it. In this way only the portion of the lamp adjacent to the slit of the monochromator was not in contact with a cold surface. This portion became just sufficiently hot to prevent condensation taking place there. The spectra in fig. 1 were photographed with a 10-foot Rowland grating, the fourth order being utilised. The line marked by a dot in the photograph is a third order line at 3391 Å.U.

§ 3. *Persistence of the Luminosity.*

The form of the silica tube used to obtain the moving column of mercury vapour is shown in the diagram. After a convenient quantity of pure mercury had been placed in it, the tube was exhausted and sealed off. The mercury placed at the beginning of an experiment in B was heated by means of a small electric heater, while the bulb C and part of the tube was kept in cold water. With this arrangement the mercury completely distilled over in about 90 minutes. The beam of ultra-violet light passed across the tube at the point A, its direction being indicated in the diagram by an arrow. A screen was so placed as to prevent any light reaching directly the cold limb of the tube. When the beam was passed across while the whole apparatus was cold the resonant radiation extended the width of the tube, but as soon as the bulb B was heated and the mercury began to distil over, the radiation became concentrated at the point where the beam entered. This resonant radiation was quite bright enough to be viewed by means of a camera with a quartz lens, using a piece of uranium glass as a screen.



A stream of green fluorescent light, originating from the concentrated patch of resonant radiation, passed round the tube with the distilling mercury vapour. A photograph of the tube under these conditions has been reproduced on Plate 4, fig. 2. This photograph was obtained by means of an ordinary camera, so that it does not show the resonant radiation, which, though of course invisible, was really more intense than the green fluorescence. The silica itself also fluoresced with a bluish-violet colour under the influence of the ultra-violet light. The effect of this has been reduced to some extent by taking the photograph through a yellow screen. Since the fluorescence of the mercury vapour is green (the region of minimum sensitiveness of the photographic plate), this operation was somewhat difficult, and the resulting photograph is not a good reproduction of the actual effect. However, it shows plainly that the stream of fluorescence passes up the tube from the point of excitation, while none passes downwards.

In the actual experiment the fluorescence clearly showed the stream-lines of the vapour passing through the patch of resonant radiation. The glow passed up the hot limb of the tube as an attenuated band, but gradually spread out and filled the whole tube as it passed into the other limb. Its course could be traced for about 18 inches, this was as long a path as it could be made to take in the particular tube used. Further investigation on this point will be made with the idea of determining the length of time for which the fluorescence will persist.

The spectrum of the fluorescence carried over was obtained by means of a small quartz spectrograph at a point some distance down the cold limb of the tube. It was found to be similar in character to the spectrum obtained by Wood for the fluorescence stimulated by cadmium light. But, instead of the two bands of continuous spectrum that Wood obtained, there were four. The 2536 line itself appeared in the fluorescent spectrum A, which is the upper one of the two reproduced in fig. 3 of Plate 4. The lower one was obtained under similar conditions except that a piece of glass was placed in the direct path of the beam, so causing the fluorescence to cease. In this way it was shown that all the lines in the upper spectrum, except the 2536 line, were due to stray light. This was deduced from the fact that in the original negative the three lines in the part of the spectrum, to which glass is transparent, were equally intense in both spectra.

This experiment also suggests a method of solving a problem raised by Wood,* in his paper on resonance radiation of mercury vapour. He attempts to discover the mechanism of the secondary resonance radiation, which surrounds the beam of primary radiation under conditions of low pressure of the accompanying air. The mercury vapour itself was of course at very low pressure, being kept at ordinary temperatures. The secondary radiation may be due, as Wood pointed out, to one or both of two causes: (1) the light from the primary beam exciting the secondary radiation, or (2) the molecules of mercury diffusing from the primary beam and being still active, exhibiting the radiation in the neighbourhood of the beam. A thin screen of quartz was used by Wood in his attempt to separate the two effects. Such a screen would allow the light, but not the molecules, to pass through. The experiment was only conclusive in as far as it showed that the greater portion of the effect was due to the action of the light radiated from the primary beam. Wood thought it impossible to obtain a screen that would cut off the light and yet would allow the molecules to pass. In effect a moving column of vapour, such as is used in the present experiment, achieves the desired object.

Certain observations during the course of the experiment seem to show that about one-twentieth of the secondary radiation in Wood's experiment was probably due to moving molecules. The rest of the radiation would be produced by scattered light from the primary beam.

§ 4. *Other Experiments.*

Besides mercury the vapours of such substances as iodine, anthracene, and retene were experimented with, in order to ascertain whether the fluorescence of the vapours persisted. An attempt was also made to obtain the same effect in the case of the fluorescence of mercury vapour excited by cadmium light. In all cases so far investigated, negative results have been obtained. This is probably due to the fact that the fluorescence does not occur at a sufficiently low pressure to make the method feasible.

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* 'Phil. Mag.,' May, 1912.

§ 5. *Summary.*

(1) The paper describes how phosphorescence of a vapour has been for the first time observed. The method consists in passing a beam of the exciting light across a moving column of the vapour. If the fluorescence of the vapour persists it will be carried along with the stream.

(2) The vapour chosen was that of mercury and the exciting light was the 2536 mercury line, obtained by means of a water-cooled silica lamp. This light caused mercury vapour to fluoresce at a very low pressure.

(3) The moving column of mercury vapour was obtained by distilling mercury in an evacuated tube. When a beam of 2536 light was passed across the moving column the fluorescence was carried along with the vapour.

(4) The fluorescence of some other vapours was also investigated, in order to ascertain whether in any case it was persistent, but no positive results were obtained.

In conclusion I have very great pleasure in thanking Prof. the Hon. R. J. Strutt, F.R.S., for his kind interest and help during the course of this research. It was at his suggestion that these experiments on the optical properties of mercury vapour were carried out.

I have also to thank Prof. Fowler, F.R.S., for kindly permitting me the use of the instruments mounted in the Spectroscopic Laboratory of the Imperial College of Science and Technology.

DESCRIPTION OF PLATE.

Fig. 1.—Showing the reversal of the 2536 line in the hot mercury lamp.
Fig. 2.—Showing phosphorescence of mercury vapour.
Fig. 3.—A. Spectrum of phosphorescence.

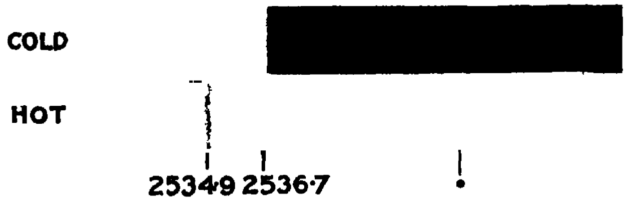

FIG. 1.

FIG. 2.

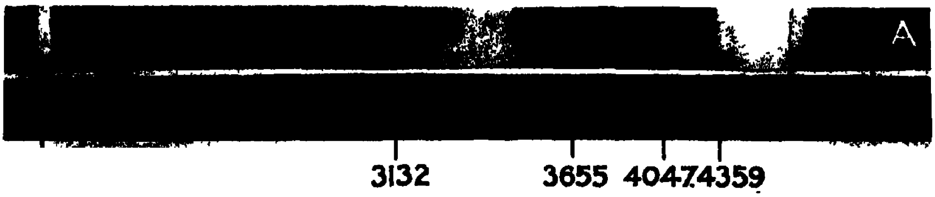

FIG. 3.

The Fluctuation in the Ionisation due to γ-Rays.

By P. W. Burbidge, M.Sc., Government Research and Jacob Joseph Scholar, Victoria College, Wellington, New Zealand.

(Communicated by Sir J. Larmor, F.R.S. Received April 21,—Read June 26, 1913.)

The work to be here considered is a continuation of a previous investigation by Prof. Laby and the present author,[*] in which the existence of fluctuations in the ionisation due to γ-rays from radium was demonstrated. In the present paper the quantitative measurement of this fluctuation is described, and its relation to the theory of γ-rays investigated.

At the present time two theories exist for the explanation of the Röntgen and γ-rays (the two radiations exhibit so many properties in common that they are regarded as phenomena differing only in degree), viz., the pulse and entity theories. According to the former, the rays are conceived as propagated from the source, with a continuous wave front, while the latter theory includes the corpuscular form of Bragg, the pulse in a tube of force, or bundle, theory of Sir J. J. Thomson, and the quantum form postulated by Planck and Stark. In any of these last theories the disturbance has a discontinuous wave front and is propagated from the source along a straight line.

Since both Röntgen and γ-rays show many points of resemblance, on the one hand, to α- and β-rays, and, on the other, to light, it becomes of importance to investigate their exact nature. More especially is this so in view of the connection that has been recently demonstrated between X-rays and light in the phenomena of fluorescence, reflection, and possibly of diffraction.

The possibility of discriminating between the two theories mentioned above by measuring the fluctuation in the ionisation due to γ-rays was pointed out by Prof. Laby[†] and by von Schweidler,[‡] and the experiments here described determine how the fluctuation varies with the ionisation:—

(1) When the solid angle of the rays used is varied.
(2) When the gas used in the ionisation vessel is changed.

The absolute fluctuation in the number of ions formed per second in the ionisation vessel, *i.e.*, Δ, has been evaluated by means of the relation established by Dr. N. R. Campbell[*] :—

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[*] T. H. Laby and P. W. Burbidge, 'Roy. Soc. Proc.,' 1912, vol. 86, p. 333.

[†] In an application made, in 1908, to the Royal Society for a grant towards the research.

[‡] E. von Schweidler, 'Phys. Zeit.,' 1910, vol. 11, p. 225.

$$\overline{\Delta^2} = 2\overline{\delta^2}C/e^2s^2R,$$

where $\overline{\delta^2}$ is the mean square deviation in millimetres of the image of the fibre of the electrometer used from its mean position, C is the capacity of the system in centimetres, R is the resistance in E.S.U. between the fibre, etc., and the earthed surroundings, s is the sensitiveness measured in millimetres per E.S.U. of voltage, e is the elementary charge in E.S.U. on an ion.

The present communication contains:—

(1) A note on the experimental arrangements.

(2) An account of the method of evaluating $\overline{\Delta^2}$, involving the measurement of δ^2, R, and s.

(3) A discussion of the results in the light of the theory developed.

(4) A criticism of some results on the same subject obtained by Dr. Edgar Meyer, of Aachen.

As these experiments will be continued the theory of them is only very briefly discussed in this communication.

Experimental Arrangements.

Most of the apparatus used in this work has already been described,[†] the essential parts, the electrometer and the ionisation vessel,[‡] being the same as were used before. It was found necessary to make several alterations and additions. The general scheme is shown in fig. 1.

A Bronson resistance was connected to the fibre of the electrometer. Some conductor, by which charges acquired by the central electrode of the ionisation vessel can leak away, is essential to enable the fluctuation to be evaluated. This previously existed in the insulation leak, which arises from the radium acting on the air surrounding the wire connecting the central electrode to the electrometer. A Bronson resistance was added as an additional conductor in order that the resistance R might not vary inversely as the ionisation in the can. The resistance consisted of two brass plates, the lower being coated with black uranium oxide, and the upper being connected to the fibre of the electrometer and air-insulated (see fig. 2). The resistance so obtained was of the order of 10^{12} ohms, and the fluctuations arising from its introduction, as shown in the photographic records, were small enough to be quite negligible.

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[*] N. R. Campbell, 'Camb. Phil. Soc. Proc.,' 1909, vol. 15, p. 117; 1910, vol. 15, p. 310; and 'Phys. Zeit.,' 1910, vol. 11, p. 826.

[†] Laby and Burbidge (*loc. cit.*). Compare figs. 1, 4, 6, 7 in this earlier paper.

[‡] The ionisation vessel had top and bottom of 2 mm. brass, sides of 0·3 mm. tin-plate, back and front and fittings of 0·6 mm. aluminium.

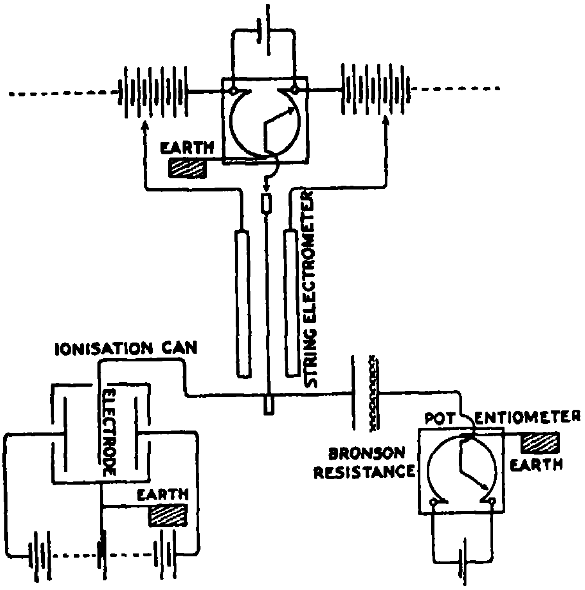

Fig. 1.—Ionisation vessel, string electrometer and Bronson resistance.

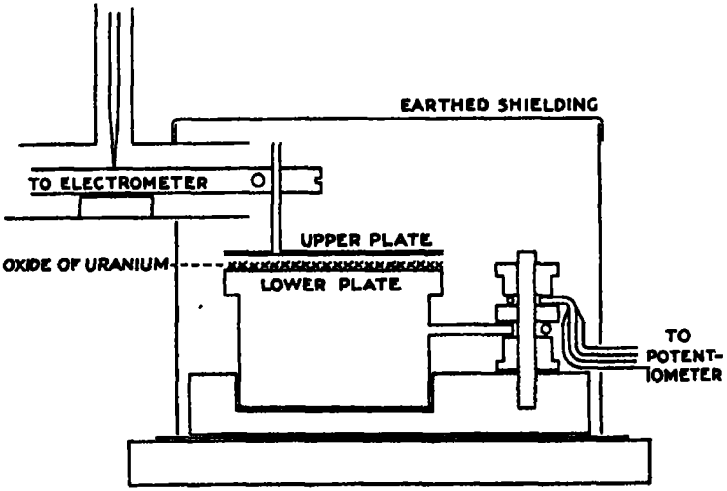

Fig. 2.—Bronson resistance.

The Source of γ-rays.—The screen surrounding the 5 mgrm. of radium was increased so as to cut off all β-rays. As determined experimentally the thickness for this was 3·8 mm. of aluminium; the equivalent thickness actually used was 4·1 mm., a thickness through which, calculating on the exponential law of absorption, only 0·5 per cent. of the fastest β-rays could penetrate.

The photographic recording apparatus was modified somewhat by the use of an extension to the bellows of the camera so that the movement of the fibre in the direction of the optic axis was not so detrimental to the sharp focus of the image, and by improvements to secure a uniform motion of the photographic film, as shown in fig. 3.

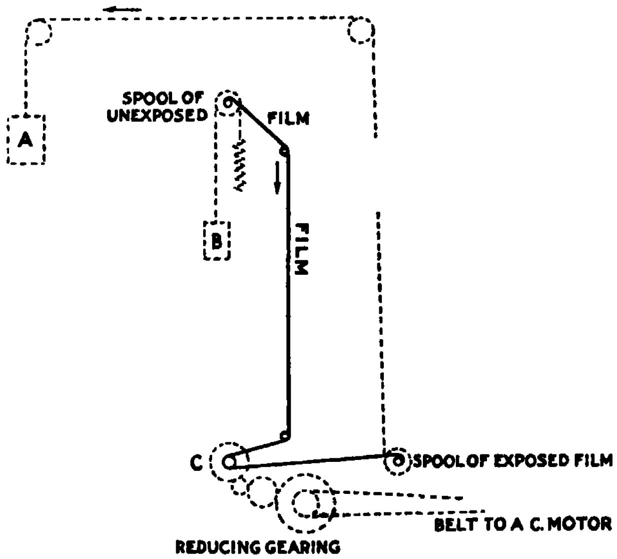

FIG. 3.—Driving mechanism for photographic film. A. Weight to keep film in tension. B. Weight giving constant resistance. C. Rubber roller round which film passes, driven through reduction gearing by A.C. motor.

Measurement of the Fluctuation.

The relation $\overline{\Delta^2} = 2\overline{\delta^2}C/e^2s^2R$ is true provided that the logarithmic decrement of the motion of the fibre is large compared to I/RC; this condition is amply fulfilled by the string electrometer used.

Since e and C are constant under the conditions used, in considering the variation of $\overline{\Delta^2}$, the corrections I/R and I/s^2 alone enter. The justification of the latter is obvious, but the former has been called in question and been proved not to hold for the quadrant electrometer.[*] For the gold leaf electroscope,[†] however, the correction has been justified and applies probably even more exactly in the case of the string electrometer. The evaluation of

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[*] E. Meyer, 'Phys. Zeit.,' 1912, vol. 13, p. 73.

[†] Campbell, 'Camb. Phil. Soc. Proc.,' 1910, vol. 15, p. 310.

$\overline{\Delta^2}$ from this expression requires the values of R, s, and $\overline{\delta^2}$ to be known. These were determined as follows:—

R was measured by finding the time required for a charge to leak through it.

Consider the theory of such a leak. If V = the mean potential on the central system in an interval of δt units; K = the mean current through R; δQ = the quantity discharged in the infinitesimal time δt; δV = the fall in potential thus produced; and C = capacity of system (36 cm.);[*] then

$$R = V/K = V\delta t/\delta Q = V\delta t/C\delta v.$$

The measurement consists in observing the time of leak (δt) of a charge over a given range (δV) of potential, about a known mean potential, V. In the observations made, V = 0·14 volt and δV = 0·01 (*c.*) on either side.

The accuracy of the method was verified by a measurement of the Bronson resistance alone, first, by allowing the charge to leak from the top plate to earth, and then by charging up the top plate through the application of a potential to the lower plate. The two methods gave concordant results.

s, the sensitiveness, was recorded by means of the potentiometer (fig. 1) on the films (see fig. 4); from these it was read in millimetres per volt.

$\overline{\delta^2}$.—The main part of each experimental observation consisted in obtaining photographic records of the variation in the potential (as shown by the fibre of the electrometer) of the central electrode. For this purpose the small contact potential of the Bronson resistance was first neutralised by the application of an equal and opposite potential to the lower plate, and then the tube containing the 5 mgrm. of radium used was adjusted symmetrically to the two compartments of the ionisation vessel (see fig. 1). Equal and opposite potentials of 200 volts were applied to the two plates —one in each compartment of the vessel—and the ionisations in the gas in these compartments finally adjusted to exact equality by means of a lead screen moved across the front of one. This adjustment was shown when the fibre, viewed from time to time for about 10 minutes, though varying continually in its reading, had its mean position approximately coincident with the zero. The saturation current, with the Bronson resistance in (which introduced no error), was then determined; this gave the ionisation, and, after the sensitiveness had been adjusted and the photographic apparatus placed in position, the film was set in motion for obtaining the

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[*] Measured by method of "mixtures," using standard cylindrical condenser with a capacity 28·4 E.S.U.

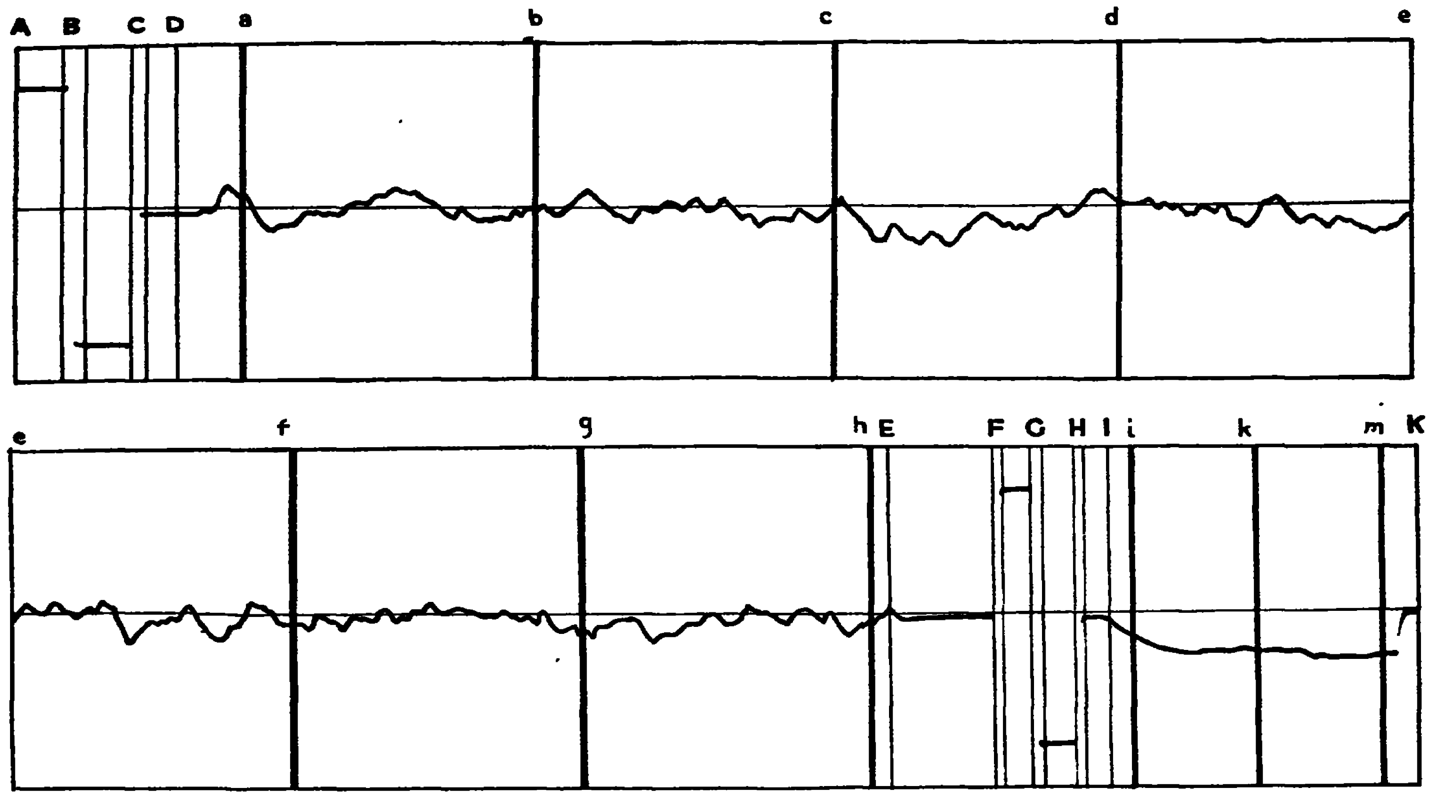

Fig. 4.—Movement of very short length of fibre recorded on moving photographic film (*cf.* pp. 49–51).

A, fibre at −0·06 volt. B, fibre put to +0·06 volt. C, fibre earthed. D, fibre isolated; radium present; fluctuations in ionisation by γ-rays recorded. *a*, *b*, ... *h*, timing signals at three-minute intervals. E, fibre earthed, speed of film decreased. F, G, and H, as A, B, C above. I, fibre isolated; radium absent; spurious fluctuations recorded (the drift seen is due to inadequate "neutralisation" of the contact potential of the Bronson resistance). *i*, ... *m*, timing signals at two-minute intervals. K, fibre earthed.

record. The order of events in taking each record (compare fig. 4), was as follows:—

Sensitiveness recorded.
Fibre earthed.
Fibre isolated (radium present) for 20 minutes.
Fibre earthed.
Sensitiveness recorded.
Fibre isolated (radium absent).

After the completion of the photographic record, the radium was replaced in position, and the resistance R determined as stated above.

A typical entry of an observation, film No. 68, reads as follows:—

Date, 16.10.12. Fibre tension in arbitrary units, 71·5.
Screen A (see below).

Gas.	Distance of Ra (cm).	Can plates (volts).	Electrometer plates (volts).	Total resistance (ohms), *i.e.*, R.	Potential on Bronson (volts).	Ionisation.
CO_2	17·3	+200 −200	+12 −12	$1·06 \times 10^{12}$	0·12	4·00 volts in 18·7, 18·8, 18·8, and 19·0; mean, 18·8 sec. = 0·21 volt/sec.

For the evaluation of $\overline{\delta^2}$ on the film, the section of it recording the fluctuation was divided into several lengths, usually seven, by the timing signals, and the mean position of the fibre in each determined by the use of a planimeter working from an arbitrary base line. The mean line for the seven points representing these mean positions was then calculated by a least squares method, and its position ruled on the film. By using a glass scale, about 120 readings of the deviation of the fibre from this mean line were taken. The mean square of these readings, $\overline{\delta^2}$, was then calculated.

Results.

The following table gives the results of the work to date; many other records have been taken but owing to ignorance of the exact conditions required for evaluation, the records are of little immediate value.

In this table, the screen A is that previously mentioned—3·6 mm. of aluminium, 0·5 mm. of glass and part of the adjustable 2 mm. lead screen. The italicised values for the total resistance in ohms in the table have been calculated from fairly accurate measurements of the Bronson resistance, and

Table I.

No.	Distance of Ra, in cm.	Gas in can.	Sensitiveness, in mm./volt.	Screen.	Resistance, in ohms.	Ionisation, in volts/sec.	Fluctuation observed, in mm.^{2}.	Fluctuation absolute.
61	2	CO_2	452	A	*0·55* $\times 10^{13}$	1·54	7·8	28·0 $\times 10^{10}$
62	17	„	388	„	*0·90*	0·23	1·2	3·0
65	2	Air	403	„	*0·60*	0·93	4·3	15·0
66	17	„	212	„	*0·95*	0·14	*0·21*	1·5
67	2	CO_2	440	„	0·64	1·39	9·5	26·0
68	17	„	347	„	1·06	0·21	1·7	4·4
69	2	H_2	492	„	0·81	0·17	*0·30*	0·5
70	2	Coal gas	397	„	0·69	0·60	2·6	7·8

a knowledge (gained from later measurements) of the leak in the ionisation vessel and the earth-shielded connections, due to the action of the radium in two positions used; the most doubtful value is that for Film 66. The last four values are more accurate, being directly measured as described above. The values of the ionisation were taken with the Bronson resistance in, as experiments showed that the ratio of the values in any two so taken was (within *c.* 2 per cent.) the same as the ratio when the Bronson was not in. The last column gives the absolute fluctuation, evaluated by means of the formula given above. The distance of the radium is given from the front end of the ionisation vessel. The italicised values of the observed fluctuation have been corrected for the spurious fluctuation in those experiments.

The above table gives the results tabulated in the order they were obtained, and they illustrate the effect of varying the distance of the radium from the ionisation vessel, and varying the gas contained in the vessel. The expressions connecting the fluctuation and the ionisation derived by Campbell* and von Schweidler† have been investigated with the object of deducing what relations are to be expected under given experimental conditions; and the results of this examination, together with the theory and assumptions on which they are based, are given in the following table. A full discussion of the theory is not given here for the reasons stated in the introduction.

Table II provides the required theoretical relations between the fluctuation and the ionisation under the experimental conditions used. It remains to be seen how the experimental results can be elucidated in this way. In

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* Campbell, *loc. cit.*

† E. von Schweidler, *loc. cit.*, and 'Phys. Zeit.,' 1910, vol. 11, p. 614.

Table II.*—Relation between the Ionisation and Fluctuation for varying Conditions.

Experiment.	$\overline{\Delta_1^2}/\overline{\Delta_2^2}$.		Theory and assumptions.
(*a*) Solid angle of rays varied	I_1/I_2	(1)	Entity theory; number of β-rays per γ-ray in ionisation vessel and *n*, number of ions per β-ray, are assumed to be independent of distance of radium from ionisation vessel.
	I_1^2/I_2^2	(2)	Pulse theory; number of β-rays formed per γ-ray in ionisation vessel, and the total number throughout "life" of γ-ray, are both assumed to be large compared to 1.
(*b*) Gas varied	I_1n_1/I_2n_2	(3)	Entity theory; number of β-rays formed in ionisation vessel per γ-ray assumed to vary with gas and to be "small."
	$\dfrac{I_1^2+I_1n_1}{I_2^2+I_2n_2}$	(4)	Entity theory; number of β-rays formed in ionisation vessel per γ-ray assumed to vary with gas, but is not "small."
	I_1^2/I_2^2	(5)	Pulse theory; same energy required to form β-ray in any gas, number of β-rays formed per γ-ray, and the total number throughout "life" of γ-ray assumed to be "large."

Table III some of the results are retabulated so as to show the effect on the fluctuation of varying the solid angle of the rays used.

(1) *Effect of Distance of Radium.*—

Table III.

No.	Gas.	Distance of radium, in cm.	Fluctuation (absolute).	Ratio of fluctuations.	Ionisation, in volts/sec.	Ratio of ionisations.
61	CO_2	2	$23 \cdot 0 \times 10^{10}$	7·7	1·54	6·7
62	"	17	3·0		0·23	
65	Air	2	14·0	9·3	0·93	6·7
66	"	17	1·5		0·14	
67	CO_2	2	26 0	5·9	1·39	6·6
68	"	17	4·4		0·21	
			Mean	7·6	Mean	6·7

The above figures indicate that $\overline{\Delta^2} \propto I$; the difference between I_1/I_2 and I_1^2/I_2^2 is large, and the mean value of the fluctuation ratio, 7·6, is sufficiently close to the mean value of the ionisation ratio, 6·7, to permit of easy distinction between relations (1) and (2) of Table II. The observations support (1) and consequently the entity theory of γ-rays.

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* The suffixes denote the variation of the quantities with the variation of the solid angle of rays or of the gas ionised. In view of the photographic evidence of C. T. R. Wilson ('Roy. Soc. Proc.,' 1912, A, vol. 87, p. 277), *indirect* ionisation alone is considered. Campbell ('Phys. Zeit.,' *loc. cit.*) has deduced the relations holding for direct ionisation; they are at variance with our experimental results.

(2) *Effect of the Gas.*—

Table IV.

No.	Distance of Ra, in cm.	Fluctuation (absolute).	A. Ratio of fluctuations.	Ionisation, in volts/sec.	B. Ratio of ionisation.
		Carbon Dioxide and Air.			
61	2	23·0	1·5	1·54	1·6
65	2	15·0		0·93	
67	2	26·0	1·7	1·39	1·5
65	2	15·0		0·93	
62	17	3·0	2·0	0·23	1·7
66	17	1·5		0·14	
68	17	4·4	2·9	0·21	1·6
66	17	1·5		0·14	
		Mean ...	2·0	Mean	1·6
		Carbon Dioxide and Coal Gas.			
61	2	23·0	3·0	1·54	2·6
70	2	7·8		0·60	
67	2	26·0	3·3	1·39	2·3
70	2	7·8		0·60	
		Mean ...	3·1	Mean ...	2·4
		Air and Coal Gas.			
65	2	15·0	1·9	0·93	1·6
70	2	7·8		0·60	

The means in the various experiments show that the ratio of the fluctuations is roughly equal to the ratio of the ionisations, but is consistently larger by about the same fraction in each case, *e.g.* A/B for the three pairs of gases has the values 1·25, 1·29, 1·19.*

The value of the fluctuation obviously differs greatly from that given by the expression $\overline{\Delta^2} \propto I^2$, and thus relation (5) in Table II, based on the pulse theory, does not hold. To distinguish between the remaining relations, (3) and (4)—both derived from the entity theory—requires a knowledge of the variation for the gases used of the number of ions formed in the vessel per β-ray, while only the ratio of the ionisation is known.

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* The result for hydrogen is not considered in this table; the values it gives for the ratio of the fluctuations agree more nearly with the relation $\overline{\Delta^2} \propto I^2$, but the degree of agreement varies widely according to the gas taken for comparison. Since the value of the fluctuation for it is the smallest, consequently constant errors of evaluation would have most effect, and, further, since the coal-gas used contains probably 40 per cent. of hydrogen and shows no such marked departure, it was considered that confirmation of the result was needed before reliance could be placed upon it in deducing theoretical relations.

In both sets of experiments, then, the evidence, though not finally conclusive on account of insufficient data, supports decisively the entity theory of γ-rays.

The result is of interest, as recent experiments tend to demonstrate that γ-rays, X-rays and light are but types of the same phenomena. If experiments now being conducted confirm the above result, an entity theory of light seems a necessary consequence.*

Dr. Meyer's Results.

Since the results obtained above do not agree with those of Dr. E. Meyer, *of Aachen*, who has been investigating γ-rays by somewhat similar methods, it is of interest to consider briefly his published results.

In a previous paper,† Dr. Meyer's earliest work‡ on this subject was criticised in certain respects; Campbell§ has also advanced some criticism on other points, and the second publication by Dr. Meyer‖ is an experimental refutation of Campbell's criticism of the method used for measuring the resistance R, between the electrometer needle and its earthed surroundings. No account is taken by Meyer of the point raised by Campbell and von Schweidler (*loc. cit.*) that the experiments, with the theory as then developed and used by him, afforded no decisive distinction between the entity and the continuous pulse theories. In a third publication,[*] the results of the previous work are taken as established, and new experiments made to ascertain if, in an ionisation vessel consisting of two similar compartments, there is any connection between the ionisation in the two sides. His results lead him to assert a connection, but the work seems open to criticism on the following grounds:—

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* [This theoretical part of the paper is criticised by a referee as follows:—

"*In the first place*, the particular form of pulse theory which is compared with the entity theory is not one which is likely to be maintained. It is assumed that on this pulse theory the number of β-rays made by one γ-ray in the ionisation chamber is not small, and is larger than the number would be on an entity theory. A pulse theory, seriously rivalling the entity theory, must suppose the number of β-rays made by one γ-ray in the ionisation chamber to be very small; and where this is done, such experiments as are made here cannot distinguish between them. The fluctuations due to variation in the number of γ-rays entering the chamber are masked by the fluctuation due to variation in the number of β-rays made by each γ-ray.

"*In the second place*, when the gas is varied, $\overline{\Delta}^2$ ought to vary as I^2 on either the pulse or entity theory. It is now clearly established that the ionisation in such a vessel as was used is due to β-rays from the walls. The fluctuations cannot depend on how these were produced, but only on the number of them, and this must be the same on either theory. In fact, n, the number of ions due to a β-ray, is proportional to the whole current; and thus in Table II (3) $I_1 n_1$ is proportional to I_1^2 or to n_1^2. This has been overlooked in the endeavour to establish a basis of experimental comparison of the two theories.

"Such experiments as are described in this paper are unable to decide between the rival theories. In this respect the author has made no advance on Meyer's work; but the criticism of that work is probably just. The fact that the present results can be interpreted in absolute measure, and shown to be of the order expected, gives them a weight much greater than previous experiments."]

† Laby and Burbidge, *loc. cit.*

‡ E. Meyer, 'Berliner Berichte,' 1910, vol. 32, p. 647.

§ Campbell, 'Phys. Zeit.,' *loc. cit.*

‖ E. Meyer, 'Phys. Zeit.,' 1912, vol. 13, p. 73.

(1) With the extreme sensitiveness of the electrometer used (10,000 mm. per volt) and the small fluctuations observed (2—14 mm.), due evidence is not given for the accuracy claimed.

(2) It is not clear that the test given by Meyer for spurious fluctuations included the Bronson resistance used; the experimental conditions would appear to prohibit this. It is known that the currents in such resistances fluctuate, and since the conductivity of the resistance used by Meyer is from five to ten times as large as the one used in the present experiments, the absolute fluctuation due to it would be larger, but the fluctuation due to the radium would be smaller than in these experiments. Unless the test for spurious fluctuations in an experiment involves *all* the arrangements used in the evaluation of the fluctuations, except that the γ-rays are absent, the experiment is open to criticism.

(3) The correction for the resistance R seems doubtful, *e.g.* in Tables VI, VII, VIII, etc., the resistance (proportional to ΔV in his paper) has almost the same value when the positive ions in both compartments are collected by the central electrode as when a differential method is used, as in our experiments. It seems obvious that a much smaller resistance is needed in the former case than in the latter, but the ΔV figures do not indicate this.

Dr. Meyer concludes:—

(1) That one γ-ray liberates more than one β-ray.

(2) That a γ-ray occupies a solid angle not small compared with that occupied by the ionisation vessel (*i.e.* a cone with vertical angle *c.* 30°).

Buchwald,[†] on the grounds of Dr. Meyer's experiments, has calculated that the probable angle of the cone of such a γ-ray is 34°.

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[*] E. Meyer, 'Ann. d. Phys.,' 1912, vol. 37, p. 700.

[†] Buchwald, 'Ann. d. Phys.,' 1912, vol. 39, p. 41.

Summary.

I. Photographic records of the fluctuations in the ionisation due to γ-rays have been obtained, and the value of the absolute fluctuation estimated from them.

II. The fluctuation has been found almost proportional to the ionisation when either the solid angle of rays used or the gas in the ionisation vessel is varied.

III. The theory evolved by Campbell has been confirmed (*a*) by the failure of six other methods of evaluation, none of which gave any constant relation between the fluctuation and the ionisation, even when all other conditions were constant, (*b*) by the concordant results obtained by using the correction factor based on his theory.

IV. Using an extension of the theory of von Schweidler and Campbell, it has been found possible to discriminate between the continuous pulse and the entity theories of γ-rays. The results appear to lead to the deduction that a γ-ray is an entity in the sense that it has a discontinuous "wave-front."

V. The work of Dr. E. Meyer on the structure of γ-rays is briefly reviewed and criticised.

The Royal Society of London lent the radium used; this, and a New Zealand Government Research Scholarship, rendered the investigation possible.

I wish also to record my gratitude to Prof. Laby for the stimulating help he has given throughout the work. My thanks are also due to Dr. G. W. C. Kaye for reading the proofs of this paper.

The Sublimation of Metals at Low Pressures.

By G. W. C. KAYE, B.A., D.Sc., and DONALD EWEN, M.Sc.

(Communicated by Dr. R. T. Glazebrook, F.R.S. Received June 10,—
Read June 26, 1913.)

(From the National Physical Laboratory.)

[PLATE 5.]

Introductory.

Many metals have been found to exhibit evidences of volatility at temperatures considerably below their melting points. As long ago as 1872, Merget* demonstrated that frozen mercury volatilised perceptibly in air in course of time. Demarçay,† in 1882, conducted similar experiments *in vacuo* and found that cadmium evaporated sensibly at as low a temperature as 160°, zinc at 184°, and lead and tin at 360° C. In 1887, Zenghelio‡ obtained evidence of the volatility of lead, copper, zinc, etc., even at room temperatures. Spring,§ in 1894, working at atmospheric pressure, showed that zinc was appreciably volatile at 300°, and cadmium and copper at 500°. Roberts-Austen and Merrett, in some unpublished experiments at the Royal Mint, in 1896, detected the volatility of cadmium and zinc at 100° *in vacuo*, while Krafft‖ in 1903 and 1905 investigated in some detail the volatilisation of a number of metals at low pressures. Rosenhain, at the National Physical Laboratory, has obtained beautiful crystals of sublimed zinc by heating a piece of zinc to 300° C. for some weeks in a glass tube containing hydrogen at atmospheric pressure.

The notable phenomena of the interdiffusion of metals, with which Roberts-Austen's name is associated, provide, of course, additional evidence of the vapour pressure that solid metals exert even at ordinary temperatures.

A familiar illustration of metallic volatilisation is furnished by the blackening of tungsten and carbon¶ filament lamps. Deposits of definite outline can occasionally be detected on the bulbs of the lamps; a fact which seems to point to the projection of particles in definite directions from the filament.

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* Merget, 'Ann. Chim. Phys.,' 1872, vol. 25, p. 121.

† Demarçay, 'Comptes Rendus,' 1882, vol. 95, p. 183.

‡ Zenghelio, 'Zeit. Phys. Chem.,' 1887, vol. 1, p. 219.

§ Spring, 'Comptes Rendus,' 1894, p. 42.

‖ Krafft, 'Ber. Deut. Chem. Gesell.,' 1903, vol. 36, p. 1690, and 1905, vol. 38, p. 254.

¶ Berthelot showed, in 1904, that such vaporised carbon is not graphitic, but amorphous.

The extent of the disintegration exhibited by a heated metal depends a great deal on its nature. In the case of the metals of the platinum group, Crookes* found that when they were heated in still air at atmospheric pressure, they arranged themselves in the following order of increasing volatility: Rh, Pt, Pd, Ir, and Ru. The marked volatility of iridium at temperatures above 1000° C. has long been known to users of platinum-iridium thermocouples.

The disintegration of a metal increases rapidly with a rise in the temperature, and almost all observers are agreed that the presence of oxygen serves to augment the effect, at any rate in those cases which have been investigated. Hydrogen and nitrogen do not, in general, favour disintegration.

The platinum metals, with the exception of palladium, all disintegrate less as the pressure is lowered, and accordingly it does not appear that in these cases the effect is one of true sublimation. Roberts† has recently conducted experiments with these metals, and infers that the volatilisation is not a simple process, but is brought about by the formation of endothermic oxides more volatile than the metals themselves.‡

With most other metals, however, we should naturally expect volatilisation to be facilitated by a reduction of pressure. We have collected in the following table, the data for a number of metals for which information

Metal.	Boiling point.		Volatilisation detectable at	Melting point at 1 atmos.
	At 1 atmos.	*In vacuo.*		
	° C	° C.	° C.	° C.
Mercury ..	357	160	−39	−39
Potassium	760	370	63	63
Sodium	880	420	97	97
Cadmium . .	778	450	160	321
Zinc	918	550	180	419
Bismuth .	1420	1000	269	269
Lead .	1525	1150	360	327
Silver .	1955	1400 ?	680	961
Copper . . .	2310	1600 ?	400	1084
Tin	2270	1700 ?	360	232
Gold	2530 ?	1800 ?	1370	1064
Iron	2450	—	950	1500
Platinum	2500 ?	—	1200	1750

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* Crookes, 'Roy. Soc. Proc.,' May, 1912, A, vol. 86, p. 461.

† Roberts, 'Phil. Mag.,' February, 1913, p. 270.

‡ In this connection, see Goldstein ('Ber. Deut. Chem. Ges.,' 1904) and Magnus ('Phys. Zeit.,' 1905, vol. 6, p. 12), who showed that Pt and Ir at a white heat rapidly absorb oxygen.

regarding the effect of pressure on the boiling point is available. The values of the higher boiling points are largely due to Greenwood.[*] Some of the volatilisation temperatures quoted have been recently determined at the National Physical Laboratory.

Columns 2 and 3 reveal the marked effect of pressure on the boiling point; and Column 4 shows the temperatures at which volatilisation has been detected, mostly at low pressures. These temperatures are intended to imply appreciable volatilisation; if the experiments were sufficiently prolonged, volatilisation could be detected in some cases at temperatures even lower than those given, as will be gathered from p. 58. Column 5 gives the corresponding melting points and is added for the sake of comparison.

Rectilinear Emission of Particles.

Evidence has recently been obtained of the emission of particles of metal at right angles to the surface of a heated metal, in much the same way, for example, as particles of metal are ejected from the surface of a cathode in a discharge tube. In most cases, this straight line emission is obscured by general volatilisation; but when the circumstances were favourable its existence has been detected.

Reboul and de Bollemont[†] have recently shown that small strips of either copper or silver, when heated in an electric furnace at temperatures from 400°[‡] to 900° C. yield black deposits which closely follow the outline of the emitting metal. Thus when the latter was cut in the shape of a cross, the deposit also was cruciform. The deposits were received on a platinum screen, and proved to consist either of the emitting metal or its oxide. In air at atmospheric pressure, 3 mm. was the greatest distance at which such deposits were obtained; the best results were obtained at about 1 mm. distance. In oxygen, the effect was enhanced; in a vacuum, the deposit gained in sharpness of outline. Curiously enough, in hydrogen, the edges of the strip seemed to be the only active regions, so that the sputtered image reproduced merely the outlines of the strip.[§]

The rate of deposition increased very considerably as the furnace was made hotter. On repeating the experiment with a sample of copper which had already been used, the deposit was much less dense than that obtained on the first heating. Other metals—nickel, iron, and aluminium—were tried, but without success.

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[*] Greenwood, 'Roy. Soc. Proc.,' 1909, A, vol. 82, p. 396; 1910, A, vol. 83, p. 483.

[†] Reboul and de Bollemont, 'Journ. de Phys.,' July, 1912, 5, vol. 2, p. 559.

[‡] Below 400° no deposits were obtained.

[§] A somewhat similar edge-effect was obtained by one of us in connection with the sputtered deposit from an aluminium cathode in a discharge tube (Kaye, 'Phys. Soc. Proc.,' Feb., 1913, vol. 25, p. 198).

Experimental.

The present authors, during the early part of last year, obtained somewhat similar results which are recounted in this paper.

Iridium.—In one experiment, with which Dr. Harker was associated,* a strip of pure iridium (S, fig. 1) was heated by the passage of a heavy alternating current of low voltage. The strip was arranged, edge upwards, within a hollow metal cylinder of diameter about 18 mm. The gas was nitrogen and the pressure about 20 mm. At the end of the experiment two horizontal bands of deposit A and B were observed on the inner surface of the cylinder, each one facing a side of the iridium strip, and of roughly the same width. The rest of the cylinder was not wholly free from deposit, but it reached a minimum at points C and D opposite the edges of the strip.

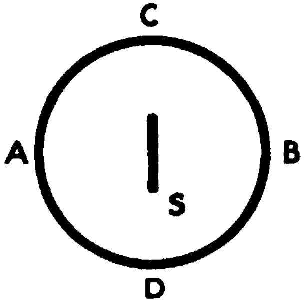

Fig. 1.

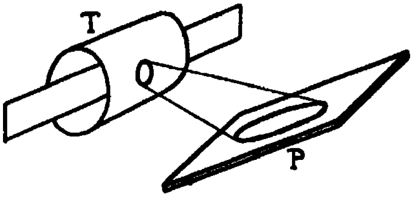

Fig. 2.

Copper.—In a second experiment, a copper tube (T, fig. 2) with a hole (diameter 8 mm.) in its side was heated from within by a strip of metal through which alternating heating current was passed. As shown in fig. 2, the strip was not in contact with the cylinder. The pressure was about 1 mm. and the gas nitrogen.

After a few minutes the copper attained a visibly red heat (800° C.), and a black deposit rapidly formed some 4 cm. away on an opal-glass plate (P) placed obliquely, as indicated in the figure. The deposit approximated in shape to an elliptical ring. This is to be ascribed to the sputtering action of the edge of the hole in the tube. The outline of the sputtered ring was shortly afterwards largely obscured by general deposit from the body of the tube and the heating strip. Fig. 3 gives a notion of the appearance of part of the elliptical band of deposit; it has been strengthened slightly in the photograph (see Plate 5).

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* See Harker and Kaye, 'Roy. Soc. Proc.,' 1913, A, vol. 88, p. 536.

Iron.—In a further series of experiments, some interesting deposits have been obtained with iron. Commercially pure Swedish wrought iron was used in the form of thin strips which were highly polished. The arrangement of the apparatus is indicated in fig. 4.

The iron strip A was mounted vertically and connected at its extremities to two stout copper leads, by which means the strip was heated electrically by direct current. Parallel to, and at about 1 mm from, the polished surface of the iron was stretched a strip of platinum foil B, in the centre of which was a small hole about 3 mm. square. A second piece of platinum foil C was welded on to B, and contained another similar hole so arranged that the two holes in B and C were opposite each other and about 5 mm. apart. A third strip of platinum foil D was mounted opposite the hole in C and about 1 mm. away from C. Strips B and C were electrically insulated from the iron strip A, and the outermost strip D, which was intended to receive the deposit, was connected to the positive end of the iron strip. The whole was placed in a vessel which was highly exhausted, and the iron strip was then heated by passing through it a direct current of about 20 to 30 ampères at 50 to 100 volts. The temperature of the iron was kept at about 950° C. for some 5 hours.*

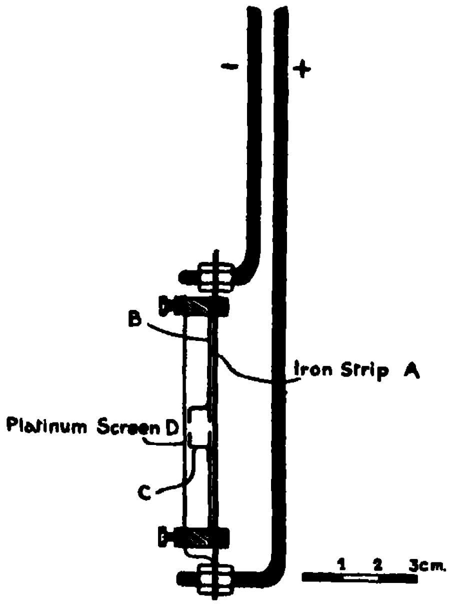

Fig. 4.

By this means, a dark brown deposit was obtained on the platinum strip D, and, as shown in the photograph (fig. 5), the deposit took the form of a well defined image of the square holes in the other pieces of foil. The clearly defined edges of this shadow make it difficult to imagine that the method of transference of the material can be other than some kind of rectilinear propagation of the volatilised particles. The slight distortion of the image is due in part to a want of alignment of the two holes in B and C, and partly to the shape of the hole in C.

No deposit was found on the sides of B and C remote from the hot iron strip. Fig. 5 shows the black deposit on the side of B facing the iron strip. There was also some deposit on the corresponding face of C around the sides of the hole; a feature which indicates that not all the particles are projected normally from the iron. In some experiments, plate C was removed and only the one hole (in B) used; the deposits in these cases were not quite so well defined.

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* The temperature was measured by a hot-wire optical pyrometer.

The surface of the emitting iron strip, when examined under a fairly high power, shows regularly oriented etched pitting (fig. 6). The method of heating by direct current seems to favour the development of these etched pits to an extraordinary degree. As described later, specimens of iron were also heated in a tube furnace *in vacuo* to the same temperature as before, viz., 950° C. In these cases, the etched pitting of the surface, although generally distinguishable, was not developed to anything like the same extent as in specimens heated under the same conditions by the passage of the heating current through the specimens themselves. It would appear, therefore, that the electrical conditions which obtain in the latter case predispose the metal to disintegration, as evidenced by the etching effects.* It would be of interest to see if heating by the passage of an alternating current through a metal would also produce such marked pitting. The frequent twinning, an example of which is shown in fig. 6, is, of course, characteristic of the structure of iron at the temperature of the experiments.

The central and hottest portion of the iron strip, which was opposite the holes in the platinum strips, was afterwards found to be brown in colour. The appearance suggested that a certain amount of oxidation had taken place in spite of the fairly high vacuum employed.† This is supported by the fact that on subsequently annealing the iron in hydrogen the brown colour disappeared and the iron reverted to its normal tint.

The deposit was found, when tested, to give a distinct iron reaction, thus proving that the shadow was due to the transference of particles from the iron. The loss in weight of the iron specimen was too small to be detected by an ordinary chemical balance. The adhesion of the deposits to the receiving strip of platinum was remarkable, vigorous polishing for some minutes being necessary for their removal. Under the microscope, the surface of the platinum where the deposit was formed shows a reticular pattern resembling the structure obtained on polished and etched metallic surfaces.

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* Fredenhagen ('Phys. Zeit.,' 1912, vol. 13, p. 539) found a parallel effect with the negative electrical discharge from a hot metal *in vacuo*. The emission from a certain electrode, when the latter was heated in an electric furnace, was only 1 per cent. of that obtained on heating by direct current to the same temperature.

† The pressure was initially of the order of 0·004 mm. of mercury and during the course of the heating averaged about 0·035 mm., the rise being accounted for by the evolution of gases from the heated iron.

As the result of a number of experiments, it was found that the maximum range of the iron particles was about 1 cm. in a good vacuum; at higher pressures it would probably be less.*

Deposits from iron were also obtained on non-metallic receiving surfaces, such as fused silica.

In order to examine more closely into the cause of this transference of material, some further experiments were carried out with iron, in which the arrangements were similar to those already described, but the heating was effected by an electric tube-furnace, wound with a spiral resistor of nichrome wire; the iron specimen did not, therefore, in this case, carry any current. The window in these experiments was a long slit parallel to and about 2 mm. from the strip; only one window was employed. As before, quite a sharp shadow of outline corresponding to the slit was obtained on a platinum screen, about 1 mm. distant from the slit. This is shown in fig. 7; the illumination of the screen in the photograph causes the grey deposit to appear white on a dark ground.

With this arrangement, one hour's heating produced only very faint indications of a deposit, whilst a clearly defined image was obtained from a run lasting three hours. With direct-current heating, on the other hand, the rate of deposition was much more rapid, and in one experiment, 10 minutes sufficed to produce a fairly clear deposit (see also p. 63).

In the tube-furnace experiment the temperature was not quite uniform, so that both iron strip and platinum screen were a good deal hotter at one end than the other. The deposit on the screen was found to be fainter at the hotter end; this was probably due to the greater loss by evaporation from the hot end of the screen. The deposit shown in fig. 7 did not possess the brown colour of the shadows obtained in the previous experiments, nor, as has already been remarked, did the surface of the iron show such characteristic etched pitting. Thus, although more prominent deposits were obtained when there was slight oxidation, it would appear that the presence of oxygen—at any rate, in quantity sufficient to cause visible oxidation—is not essential to the process of transference.

Tungsten.—Extensive deposits and corresponding shadow results were also obtained when tungsten was heated *in vacuo* to about 1800° C.

Discussion.

From the foregoing results, and those obtained by Reboul and de Bollemont, it would appear that there are two main classes of vapour given out when a metal volatilises; one kind, which is associated with evaporation as usually understood by the term, the other, made up of particles of metal, which travel in straight lines from the surface of the metal, which they leave approximately at right angles, and which, as our experiments appear to show, have (in the case of iron, at any rate) a range of only a centimetre or so *in vacuo.* What may be the inherent cause of difference between these two kinds of particles we are not in a position to say at present; we suggest that the "rectilinear" type consists of electrified particles of metal, while the ordinary vapour particles are electrically neutral.

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* *Cf.* Reboul and de Bollemont, above.

It is well known that, if a liquid has its surface suddenly changed in area, a surplus charge of electricity makes its appearance, as, for example, in the splashing of water or mercury. On the same grounds, the pitting of the heated surface, and the consequent alteration of area, would be expected to release a certain amount of electrification, which would, in favourable cases, accompany the liberated particles. The repulsion of the charged particles at right angles to the surface of the heated metal would follow if the surface were also charged with like sign; this, of course, is possible with a strip heated by direct current. We have already remarked on the special efficacy of direct current in producing deposits.

The effect is not so easy to explain in the case of the tube-furnace and alternating-current experiments. Reboul and de Bollemont suggest, in explanation of the phenomena, that the transference of the material is due to miniature eruptions caused by the explosive combination of occluded hydrogen and oxygen in the metal. On this view, the effect would be expected to fatigue, and this is in accordance with their experiments (p. 60). The explanation does not, however, seem to us convincing.

In our experiments with iron, the temperature did not exceed about 1000° C., under which conditions we should expect that any electrified particles there might be would carry a positive charge; and, in fact, Sir J. J. Thomson* showed some years ago that positively charged particles of metal were among the positive ions given off by platinum heated to moderate temperatures at low pressures. It would be interesting to see if a difference could be detected in the intensity of the deposits obtained from either end of a strip of metal heated by direct current. On the above hypothesis, the positive end of the strip might give an appreciably heavier deposit at such temperatures.

At higher temperatures than we have employed—near and above the melting point of iron—negative electricity predominates, and opposite results would accordingly be expected in such an experiment. The effect of a magnetic field on the stream of particles would, of course, be a valuable piece of evidence. By such means, Owen and Halsall* find, however, that in a good vacuum, and over a wide range of temperatures all high enough to give negative ionisation, the thermionic current, in the case of Pt, Pd and Ir, is due almost entirely to electrons. They conclude that the proportion of heavy and metallic negative ions is certainly less than 1 part in 2000. It should be remarked also that Roberts, in the paper already referred to, did not find any evidence of particles which were electrified in the vapours of the platinum metals. But, from his published account, we should gather that the fog-condensation chamber, by which he tested the point, was probably too remote from the heated metal to detect such short-range particles as we have described.

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* 'Conduction of Electricity through Gases,' 1906, p. 217.

The influence of traces of oxygen in producing a kind of "weathering" of the surface of the metal is one on which stress has been laid by a number of experimenters, and it is reasonable to suppose that some such action would augment the disintegration to a marked degree with some metals. It is significant that most workers are agreed that the presence of oxygen accentuates the positive electrical emission from hot metals; in such cases we may regard the charged particles as the direct outcome of the energy of reaction between the metal and the gas. We have elsewhere noted Roberts' conclusions as to the part played by oxygen in the volatilisation of the platinum metals, and it is a matter for further investigation to ascertain the extent of the effect with the baser metals. Some evidence is afforded by the experiments on p. 64.†

As an alternative to the charged-particle hypothesis it is not impossible that the distinction between the "rectilinear" particles and the ordinary particles is one chiefly of size. We should expect that very small emitted particles of metal—with dimensions not far from molecular—would suffer appreciable scattering by the gas molecules and lose very speedily their original direction of projection. But larger particles, projected with the same velocity, would travel farther before being similarly disturbed. Possibly the range of the projected particles under the same temperature conditions varies considerably from metal to metal; and this may account for the lack of success which attended Reboul and de Bollemont's efforts to obtain deposits with metals other than copper and silver at atmospheric pressure.

It may not be too far from the purpose of this paper to consider the possible source of such large particles. Dr. Rosenhain and one of us‡ have

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* 'Phil. Mag.,' May, 1913, vol. 25, p. 735.

† See also Humfrey, 'Iron and Steel Inst. Journ.,' 1912, Carnegie Memoirs.

‡ "Intercrystalline Cohesion in Metals," Rosenhain and Ewen, 'Inst. Metals Journ., Sept., 1912,

Fig. 3. Copper Deposit

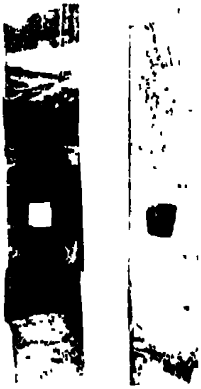

Fig. 5.—Photograph of Hole and Iron Deposit cast by it.
In the above figure, plate C is behind plate B. Full size.

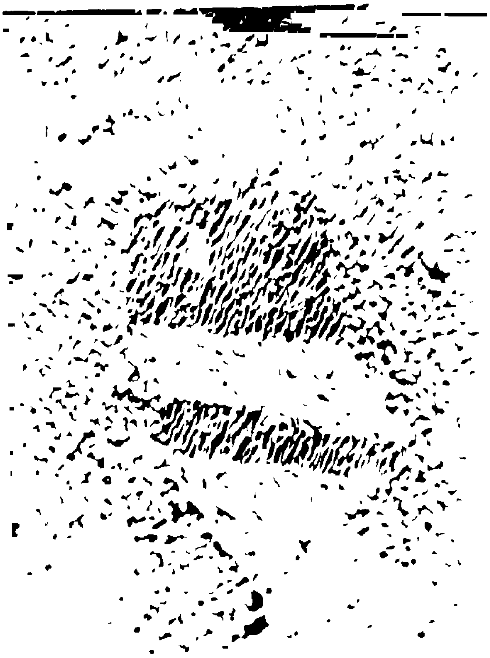

Fig. 6.—Pitted Surface of Iron Strip. × 500 diameters.

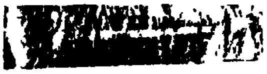

Fig. 7.—Iron Deposit. ½ full size.

put forward a theory as to the mechanism by which evaporation takes place from crystalline metals. The view was adopted, from the observations of the behaviour of a number of metals *in vacuo*, that the volatilised metal consists initially of the intercrystalline amorphous material which cements together the crystal faces. This amorphous cement is more volatile than the crystals themselves, and accordingly grooves or channels are formed along the crystal boundaries of metals subjected to prolonged heating *in vacuo*. The increased liability to erosion along the sides of these channels may perhaps be the cause, directly or indirectly, of particles larger than those from the body of the crystals. With polished specimens the channels are visible under the microscope; the process is known as vacuum etching.

If there is any real analogy between the sputtering from a cathode in a low-pressure discharge tube, and thermal sputtering such as we have described, it may be that cathodic sputtering carried out under suitable conditions would similarly lead to the formation of patterns corresponding to the structure of the metal.

So far as evaporation from the crystals themselves is concerned, we may usefully employ the conception of a "crystal unit" adopted by some metallographists. The term implies a small ordered stable aggregate of molecules which serves as a brick from which to build up the crystal structure. We may imagine that either through the application of heat or by chemical combination the stability of a surface unit is endangered by reason of the loss of individual outlying molecules. The whole unit disintegrates and comes away piecemeal from the crystal in particles, may be, of appreciable size, and at the same time a pit is commenced in the crystal surface. We should not be unreasonable in expecting that such particles coming from a stable crystal system would be electrically charged, in contradistinction to those coming from an unordered amorphous medium.

The results described in this paper are to be regarded as of a preliminary character; it will be apparent that there is scope for further work in a number of directions.

A Peculiar Form of Low Potential Discharge in the Highest Vacua.

By the Hon. R. J. STRUTT, F.R.S., Professor of Physics, Imperial College of Science, South Kensington.

(Received June 18,—Read June 26, 1913.)

Mr. C. E. S. Phillips has described a curious electrical effect.* Iron electrodes E_1, E_2, fig. 1,† were fixed in a glass bulb as shown. The bulb was exhausted very highly; a discharge was passed for a moment, and turned off. The iron electrodes were then magnetised by exciting the electromagnets M_1, M_2. On magnetisation, a luminous ring was observed in the equatorial plane of the magnet, which lasted for a few seconds, and then died out. The effect excited considerable interest at the time, and careful experiments were made by the discoverer to elucidate its causes. The following may be quoted from the concluding section of the paper as representing his views.

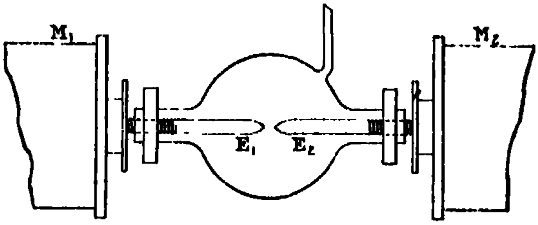

FIG. 1.

"The preceding experiments show that the principal effect of the magnets is to produce a concentration of negative ions at the strongest portion of the magnetic field, and centrally within the bulb. . . . . I consider that this concentration of negative ions is due to two main causes. In the first place it is partly produced by the action of the magnetic field on ions already in motion within the bulb. . . . . And secondly owing to the reaction resulting from the sudden excitation of the magnets, the comparatively dense cloud of ions situated at the ends of the bulb would, in rapidly turning about the magnetic axis, tend to move towards the pointed end of the electrodes, and so concentrate as observed."

I find some difficulty in forming a clear idea of the theory here suggested but the effects are apparently attributed to ions left in the volume of the bulb, and to the electromotive force set up by the sudden growth of the magnetic field. The latter point of view was favoured by Prof. S. P. Thompson* and by Lord Kelvin,† but the experiments described below cannot be reconciled with it, or with the idea that ions left in the gas by the preliminary discharge have anything to do with the phenomena.

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* 'Roy. Soc. Proc.,' 1898, vol. 64, p. 172; 'Phil. Trans.,' A, 1901, vol. 197, p. 135.

† This figure is taken from Phillips' paper.

In other passages Phillips attaches importance to charges of electricity left on the glass walls by the preliminary discharge. In this, as I hope to be able to show, he is entirely right.

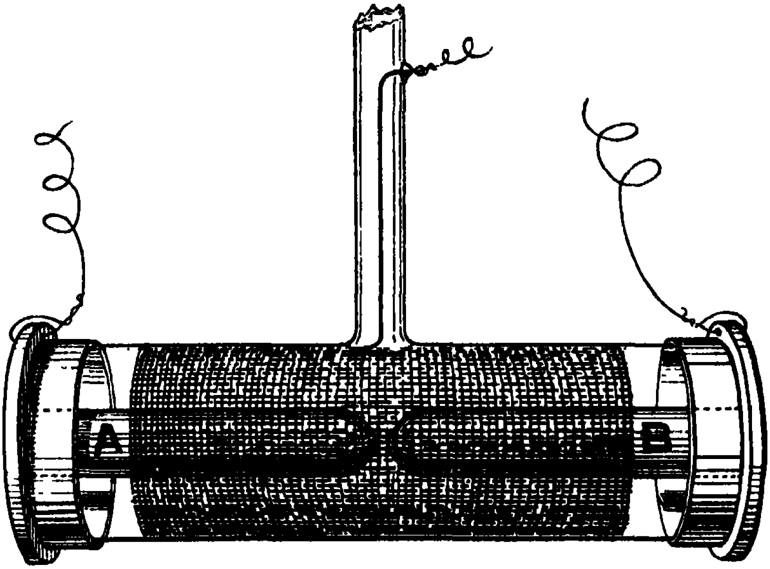

Fig. 2.

To test the latter question, it was decided to repeat the experiments in a vessel lined internally with wire gauze, thus avoiding the uncertainty always encountered in experimenting with charged insulators. The vessel employed is shown in fig. 2. The gauze lining was separated from the iron poles by a short length of glass, and communicated with the outside by a wire so that it could be brought to any desired potential. The vessel was highly exhausted by a Gaede pump followed by cooled charcoal. An induction coil was connected to the end caps A, B. The coil circuit was insulated, and the gauze lining connected to earth. The coil discharge passed with difficulty, with occasional flashes of green phosphorescence. It sufficed to pass it for a moment only. Then, when the electrodes were magnetised, the equatorial ring described by Phillips appeared extending as far as the gauze sheath. It lasted 3 seconds or more and then became visibly intermittent, finally ceasing. If the gauze sheath was electrically connected with the pair of poles AB, the ring was instantly extinguished, no trace of it remaining.

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* 'Electrician,' 1890, vol. 43, p. 412.

† 'Electrician,' 1899, vol. 43, p. 532.

This experiment makes it certain that the ring is essentially connected with a difference of potential between the inner walls of the vessel and the pair of iron electrodes. The potential difference must be attributed in this case to a charge left on the electrodes, and on the coil circuit connected with them, since the gauze lining is earthed.

Since a charge on the iron poles was necessary, it was an obvious step to maintain it by means of an electrical machine. When the iron poles (connected together) were kept negatively electrified in this way, the ring could be maintained indefinitely. It was extinguished when the magnet was turned off, but reappeared when the magnet was turned on again, and then remained steady. It is therefore evidently unconnected with induced electromotive forces produced during establishment of the magnetic field.

The preliminary induction coil discharge was not necessary. The ring could be started at any time without it.

Finally, no ring was obtained when the iron poles were positively electrified.

Measurements of the potential difference between the iron poles and the gauze lining when the ring was formed showed that this only amounted to about 300 or 400 volts, varying somewhat with the exact conditions. When the magnet current was turned off this potential difference at once leapt up to a very high value, far above the capacity of the measuring instruments available (12,000 volts).

The experiments just recorded indicate the following proximate explanation of Phillips' phenomenon. The preliminary induction coil discharge serves only to leave a static charge of electricity on the glass walls, or, if the induction coil circuit is nowhere earthed, on the electrodes. Under ordinary conditions the electricity thus left is far from being able to discharge itself through the highly rarefied gas. But when the magnetic field has been created its escape is very much facilitated. The luminous ring indicates discharge.

That the discharge lasts some seconds is probably to be explained by the well-known gradual leaking out of the electric charge from insulators. In the modified form of experiment with earthed gauze walls the charge is on the iron poles and on the secondary circuit of the Ruhmkorff coil (not in action). The capacity is mainly in the condenser formed by the insulating tube on which the secondary is wound, the primary and secondary acting as coatings. The charge of this condenser leaks out gradually, owing to "electric absorption."

The question next to be faced is why the discharge potential is so enormously reduced by excitation of the magnets.

With the conical pole pieces so far used, it is difficult to determine whether the effective component of the magnetic force at the electrode surface is parallel to the lines of electric force, or perpendicular to them. A piece of brass tubing was slipped over the pole pieces as indicated in fig. 3, connecting them electrically, but not, of course, magnetically. The low potential ring discharge was equally well obtained in this case, starting from the portion of the brass tube midway between the poles. The lines of electrostatic force are with this arrangement necessarily radial to the brass tube, and the lines of magnetic force in the equatorial plane are at right angles to them, as indicated by the dotted lines.

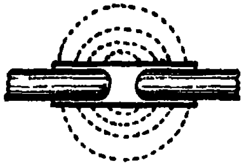

FIG. 3

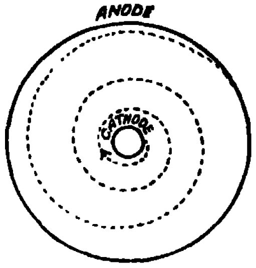

FIG. 4.

Let us consider what will be the path of an electron starting from the brass tube, used as cathode. If the electric force alone were acting, the electron would, of course, go radially outwards towards the anode, which is concentric with the brass tube. When, however, a transverse magnetic force acts as well, the electron will be deflected from its initial path, and will tend to curl round the brass tube from which it started, at the same time as it moves outwards under the influence of the electric force. The resultant path will therefore be a spiral[*] and the electron will perhaps cross the radius of the cathode along which it started several times (fig. 4) before reaching the anode.

In an ordinary vacuum discharge, without magnetic force, electrons starting from the cathode are not able to ionise the gas until they have travelled a certain distance, represented by the Crookes dark space. Why this should be so, and, in particular, why the region of ionisation (*i.e.* the negative glow) is suddenly entered, is hard to understand. Accepting it however, as a fact, we can in a measure foresee the action of magnetic force with this disposition of electrodes in lowering the discharge potential. The gas space in the neighbourhood of any element of area on the cathode is continually crossed by electrons from elements of area at some angular distance away round the tube; electrons which have already travelled some distance through the gas possibly in circulating more than once right round the cathode. They, at any rate, are able to ionise the gas, and consequently to lower the potential gradient. Thus the Crookes dark space, the un-ionised region in which the great expenditure of electromotive force occurs, is almost abolished, and the discharge potential drops accordingly.

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[*] The form of this spiral could be calculated *à priori* if we regarded the motion as free and made simple assumptions as to the radial distribution of the electric and magnetic forces. But it is, of course, useless to regard the distribution of electric force as undisturbed by the passage of the current,

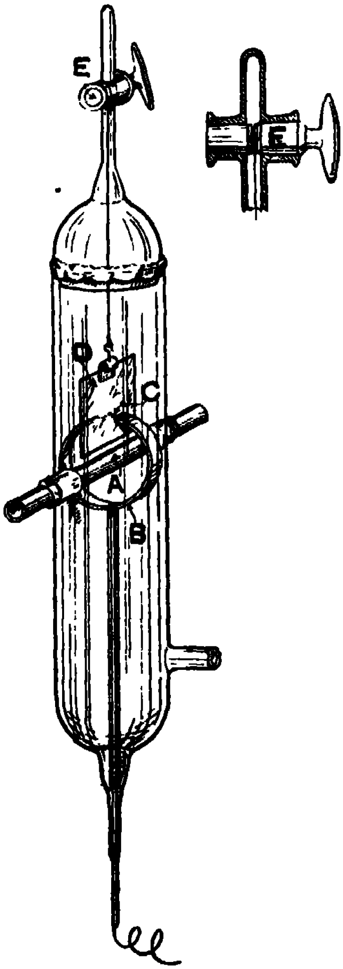

Fig. 5.

Discharges of this kind can be conveniently maintained by a battery of say 300 cells, a telephone in the circuit is quite silent, unless the current exceeds a certain limit.

Additional and Confirmatory Experiments.

The spiral path of the electrons is clearly indicated by theory, and affords as satisfactory an explanation as can be expected of the great diminution of voltage drop at the cathode, having regard to the general level of our comprehension of such phenomena.

No spiral structure can be seen in the luminous effect, nor is it to be expected, since everything is symmetrical about an axis. The spirals starting from different azimuths round the cathode overlap, the aggregate thus produced having circular symmetry.

We can, however, prove that the paths of the electrons have a tangential component by simply interposing a radial partition which stops tangential motion, though it does not interfere with direct passage of ions between the electrodes. The low potential discharge then fails, and we can only force the current through at the enormous electromotive forces ordinarily required in high vacua.

Fig. 5 shows the arrangement. The brass tube A contains inside it the magnet poles (not shown) about 1 cm. apart, separated by a brass distance piece. The tube is cemented airtight right through the glass envelope and serves as cathode. Its interior, however, is independent of the vacuum, so that the distance between the poles can be adjusted without difficulty. The concentric ring anode B, 4·5 cm. in diameter, is slit at *c* to admit the mica slip D. D can be lowered by means of a thread from the winch E, which can be operated from outside.*

On lowering the mica slip, the effects are as follows: At first the rise of potential is small, not exceeding a hundred or two volts until the mica is half-way down. It then begins to increase more rapidly until, when 2 or 3 mm. off the brass tube, it has risen to 1000 volts. Finally, when nearly touching, the potential suddenly leaps up until capable of sparking 2 or 3 inches in air; this stage is conveniently demonstrated by an induction coil, though the steady voltage of an electrical machine or battery is necessary when the lower voltages are to be measured.

These changes in the discharge potential are accompanied by interesting luminous effects. In the absence of the radial partition, the whole space between the electrodes in filled with luminosity. As the mica descends, it cuts off the light in the sharpest and clearest manner from the whole circular ring into which it protrudes. Beyond this limit nearer the centre, the luminosity remains unaffected (fig. 6). The experiment proves most definitely that the circular movement of electrons ordinarily prevails as far

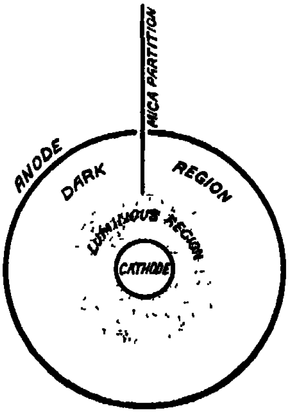

FIG. 6.

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* The winch is constructed by filing a groove for the thread round the plug of an ordinary stopcock; this arrangement is copied from one devised by Mr. Aston for Sir J. J. Thomson's experiments on positive rays.

out as the anode ring. At the same time the character of the discharge is not fundamentally altered, unless circular movement in the immediate neighbourhood of the cathode is prevented.

When this occurs, the mica partition being right down, no more luminosity is to be seen in the gas, and green phosphorescence of the glass envelope, previously absent, suddenly becomes intense.

Summary.

The phenomenon originally described by Mr. C. E. S. Phillips is traced to its origin.

As an outcome of this a peculiar form of electric discharge is studied. The cathode is a cylinder immersed in a magnetic field parallel to itself. The anode is a ring concentric with the cathode. In very high vacua the electrons travel from cathode to anode in a spiral path, whirling round the cathode. The drop of potential over the cathode region is reduced from, say, 200,000 volts to 300 volts.

Further investigations are in progress, including the detailed study of potential gradient in these discharges at various gas densities.

On the Efficiency of Selenium as a Detector of Light.

By E. E. FOURNIER D'ALBE, D.Sc. (Birm.).

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The following investigation concerns the limits up to which minute quantities of light and minute variations of its intensity may be discovered by means of selenium.

There are two actions of light on selenium which may be used—(1) a change in the conductivity, first described by W. Smith in 1873; and (2) the generation of an E.M.F. in a voltaic cell in which selenium is an electrode (Sabine, 1878).

The efficiency of an apparatus for the detection of light is the ratio of the amount of measurable effect it indicates to the amount of light received by the apparatus. Both the above actions being static, the amount of light available is best stated in terms of the steady flux of light, the unit being the lumen, or the amount of light falling upon 1 sq. m. distant 1 m. from a source of 1 candle-power.

Hitherto it has been customary to specify the "sensitiveness" of a selenium preparation by stating the ratio in which its resistance is reduced by a given illumination, reckoned in metre-candles ("lux"). This practice, however, gives no indication regarding the useful effect to be obtained from a restricted amount of light, such as that spreading out conically from a star image, as this depends upon the extent of the sensitive surface to be covered. Since the effect obtainable with a given selenium preparation is directly proportional, as a rule, to its sensitive surface, the latter has to be taken into account in determining its efficiency, and this is done by specifying the light in lumen rather than lux.

The Voltaic Efficiency.

Selenium "cells," properly so called, are electrolytic cells in which the illuminated selenium forms one of the electrodes and generates an E.M.F. Their efficiency should be defined as the E.M.F. in volts generated per lumen when the illumination is 1 lux. The illumination must be specified, since the E.M.F. is proportional to the square root of the incident energy.

Thus, in the arrangement adopted by Minchin[*] for the selenium photometry of stars, 0·03 volt was obtained by illuminating a sensitive surface of 0·645 sq. cm. by means of a candle at a distance of 274 cm. The illumination was 0·133 lux. With unit illumination, the E.M.F. would have been 0·0822 volt. Then the flux of light intercepted by 0·645 sq. cm. would have been 64·5 microlumen, and the resulting voltaic efficiency is 1270 volts per lumen.

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[*] G. M. Minchin, 'Roy. Soc. Proc.,' 1895, vol. 58, p. 142; and 1896, vol. 59, p. 231.

The Galvanometric Efficiency.

Selenium "cells" in which the action due to light is a change in the resistance of selenium are more properly termed selenium "bridges" (Minchin). The problem here presented for solution is not so much to obtain the largest possible ratio of "dark" to "light" resistance, but the largest absolute increase of conductivity, *i.e.* the largest additional *current* on exposing to light. In this respect, the most "sensitive" bridges may be comparatively useless unless they also have a reasonably low resistance, and this it has always been found difficult to secure.

The "galvanometric efficiency" may be defined as the increase of conductivity produced in a selenium bridge under unit flux of light. Convenient numbers, applicable to most bridges made, are obtained if the conductivity is reckoned in reciprocals of megohms ("micromhos") and the flux of light in lumen. Thus, a selenium bridge 10 cm. square, placed at 1 m. from a 100 candle-power source, would receive 1 lumen of light. If, under those circumstances, its resistance changed just as it would if a megohm were connected in parallel with it, its "galvanometric efficiency" would be unity.

Observed Efficiencies.

The data hitherto published with regard to the results obtained by means of selenium preparations are often insufficient for determining their efficiencies. M. Reinganum,[*] using photo-voltaic selenium cells with a sensitive surface of 5 9 sq. cm., obtained about 0·12 volt with a Nernst lamp placed at 30 cm. This gives a voltaic efficiency of about 6 volts per lumen at normal illumination if the square root law holds good for intense illuminations. Low as this efficiency is, it is probably considerably above that obtained by v. Uljanin[†] in 1888, who observed 0·12 volt in sunlight (about 50,000 lux).

As regards galvanometric efficiencies, the greatest interest, from the point of view of the present investigation, attaches to the figures given by Stebbins,[‡] who recently studied the light-curve of Algol by means of a selenium bridge. The light from the star was received by the 12-inch objective of a refractor, and an extra-focal image 0·7 cm. in diameter was formed on a Giltay selenium bridge having a "dark" resistance of 3 megohms. The illumination due to the star was thus increased 1,900 times. Now, the illumination due to Arcturus is very nearly one microlux*. The stellar magnitudes of Arcturus and Algol at maximum are given by the Nautical Almanac as 0·3 and 2·2 respectively. Hence the "unaided" illumination by Algol will be 0·174 microlux, and the illumination of its extra-focal image 330 microlux. This illumination, falling on a surface of area 0·385 sq. cm., gives a light flux of 0·0127 microlumen.

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[*] M. Reinganum, 'Phys. Zeitschr.,' 1906, vol. 7, p. 786; and 1907, vol. 8, p. 293.

[†] v. Uljanin, 'Wied. Ann.,' 1888, vol. 36, p. 241.

[‡] J. Stebbins, 'Astrophys. Journ.,' 1910, vol. 32, p. 185.

The deflection shown by the galvanometer was 8 divisions. The deflection represented a current of $1{\cdot}92 \times 10^{-9}$ ampère. The voltage used was 6. Hence the additional conductivity was 0·00032 micromhos, and the "galvanometric efficiency" was 25,200 micromhos per lumen.

That a galvanometric efficiency of 25,200 is unusually great will appear from a calculation of the efficiency of a cylindrical bridge described by Ruhmer† as the best out of a number of bridges tested. The area exposed to an illumination of 4·6 lux was 14·2 sq. cm., giving a flux of 0·00653 lumen. The resistance fell from 35,000 ohms to half that value, which means an additional conductivity of 28·6 micromhos. Hence the efficiency is 4380 micromhos per lumen.

Another Ruhmer bridge, used by Korn‡ for picture-telegraphy, had an efficiency of about 234 micromhos per lumen in "diffused daylight" (about 1,000 lux).

Conditions Affecting the Efficiency.

In order to compare two selenium bridges under standard conditions, it is necessary to take into account a number of circumstances affecting their indications. These are the following:—

(a) *Colour.*—For the ordinary sources of light, the maximum effect shown by selenium is that due to the visible red, and as the maximum shifts with the distribution of energy in the spectrum, this distribution must be specified.

In practice, it will be most convenient to adopt a standard distribution of energy in the spectrum, such as is offered by one of the accepted standards of brightness. I suggest, as the standard illumination, that provided by the whole spectrum of Harcourt's pentane standard, the distance from the source being such as to give one lux. As an alternative, the Hefner lamp might be adopted.

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* G. M. Minchin (C. V. Boys), 'Nature,' 1895, vol. 52, p. 246. See also G. Müller, 'Die Photometrie der Gestirne' (Engelmann, Leipzig).

† E. Ruhmer, 'Phys. Zeitschr.,' 1902, vol. 3, p. 468.

‡ A. Korn, 'Phys. Zeitschr.,' 1904, vol. 5, p. 113.

(b) *Temperature.*—Stebbins[*] found that the sensitiveness of a selenium bridge was considerably increased by lowering its temperature permanently to 0° C. Pocchettino[†] found a reduction of 25 per cent. in the sensitiveness on plunging a bridge into liquid air. I found a reduction of 10 per cent. under the same circumstances.[‡] I propose to adopt 15° C. as the most convenient standard temperature, freezing point being unsuitable for photo-voltaic selenium cells.

(c) *Voltage.*—The resistance of a selenium bridge depends upon the voltage, the percentage decrease of resistance being proportional to the logarithm of the applied voltage.[‡] I propose 1 volt as the standard voltage. This has the advantage that the efficiency can be expressed in micro-ampères (instead of micromhos) per lumen. The voltage does not sensibly affect the sensitiveness, unless it is so high that the Joulean heating produces a perceptible rise in the temperature of the bridge, whereupon the sensitiveness decreases.

The wide divergence of results hitherto obtained with regard to the "sensitiveness" of selenium is attributable to the differences in method of exposure and of interpretation. The measurements are affected by the "inertia" of selenium, shown in the slowness with which it acquires its final conductivity when illuminated, and the even greater slowness of recovery in the dark.

In selenium bridges with graphite electrodes, in which there is no chemical action between the electrodes and the selenium, the changes of conductivity during and after faint illumination closely approximate to what they would be if due to a progressive ionisation of the selenium under the action of light, the number of ions produced in unit of time being proportional to the flux, and the total number proportional to the total quantity of light, less whatever ions recombined. The equation to the light-action curve is then

$$dN/dt = C - BN^2,$$

where C is proportional to the flux of incident energy and B is the coefficient of recombination. N is the additional conductivity, and is proportional to the number of ions of both signs liberated. In a steady state $C = BN_0^2$, or the final steady conductivity N_0 is proportional to the square root of the light intensity (as actually found by Rosse, Adams, Borndt, and Minchin).

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[*] J. Stebbins, *loc. cit.*

[†] Pocchettino, 'Rend. R. Accad. dei Lincei,' 1902, vol. 11, p. 286.

[‡] E. E. Fournier d'Albe, 'Roy. Soc. Proc.,' 1912, A, vol. 86, p. 452.

By integration we get

$$N = \sqrt{(C/B)}\tanh(t\sqrt{C}),$$

or

$$t = \frac{1}{2BN_0}\log\frac{N_0+N}{N_0-N}.$$

The tanh-curve has an initial straight line portion inclined to the N-axis, so that before recombination becomes considerable the change of conductivity on illumination is proportional to the incident energy, as is found to be the case for all feeble exposures.

For the recovery curve we have, by integrating $dN/dt = -BN^2$, the relation

$$\frac{1}{N} - \frac{1}{N_1} = Bt,$$

where N_1 is the additional conductivity at the moment of shutting off the light. N_1 may be most conveniently obtained from the recovery curve itself. If the galvanometer deflection at the moment of obscuration is called zero, and d_1, d_2 are two readings taken at equal time-intervals after that moment, then

$$N_1 = \frac{d_1 d_2}{2d_1 - d_2}.$$

This N_1 is the final value attained by the recovery after a very long time. It is hereinafter called the "total recovery," and designated by R. It is, other conditions being equal, the net additional conductivity due to previous illumination, whatever may have been the method of exposure. But since the rapidity of reaction varies greatly with the intensity of the light, it is best to adopt a method of exposure in which the light action has a definite relation to the recovery. This is attained by alternately exposing and obscuring for equal times until the curve oscillates between steady values. Then the number of ions produced by illumination is twice the number recombined in the same time, and if the number produced varies as the incident energy, the amplitude of oscillation will also vary as the incident energy. This is shown below to be very approximately the case.

Thus the process proposed for determining the true increase of conductivity for a given illumination is the following:—

Illuminate and darken for alternate periods of one minute each, and when the " light " and " dark " deflections have each become consistent, shut off the light finally and take readings after the first and second minute.

The conditions proposed for determining the normal galvanometric efficiency of a selenium bridge may here be summarised:—

(*a*) Quality of light: complete radiation from a standard pentane lamp.
(*b*) Illumination: 1 lux.
(*c*) Voltage: 1 volt.
(*d*) Temperature: 15° C.
(*e*) History: alternate light and darkness for one minute each until steady state is attained.
(*f*) Measurement: readings for successive minutes during recovery. Evaluation of the "normal galvanometric efficiency" in micromhos per lumen, in this case equivalent to micro-ampères per lumen, or micro-ampères per square centimetre of sensitive surface, divided by 0·0001.

The Detection of Small Fluxes of Light.

A preliminary experiment to test the efficiency of selenium in detecting small fluxes of light was made as follows:—A thin rod of highly insulating porcelain was ground flat at one end, offering a circular surface 0·1 sq. cm. in area. Thick pencil lines were drawn along two opposite generators of the cylindrical surface, and a cap of selenium was thinly spread over one end. The selenium was then sensitised in the usual manner by annealing, and the rod was inserted in a hole bored through a stick of ebonite, and fixed by means of binding screws When not exposed, the selenium was covered with a cap fitting over the aperture. This miniature selenium bridge is shown in fig. 1. Its resistance, when freshly prepared, was 50 megohms.

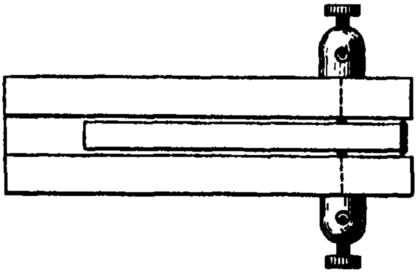

Fig. 1.

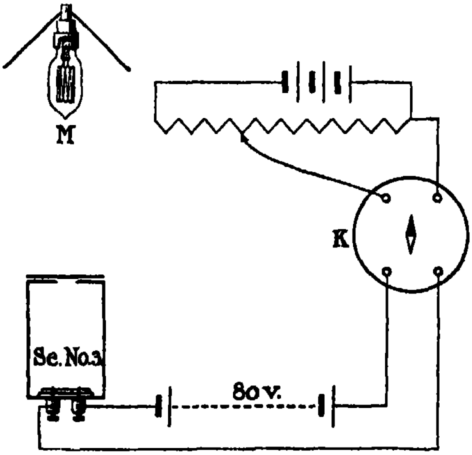

Fig. 2.

It was inserted into a circuit containing a battery of 20 volts and a Broca (consequent pole) galvanometer giving 0·6 division for 10^{-9} ampère. The "dark" deflection was compensated by suitably altering the magnetic field, and the selenium was then exposed to various moderate illuminations. The faintest illumination discoverable with certainty proved to be that due to a paraffin candle 5 m. from the selenium. This illumination was 0·04 lux, and the light flux received on the sensitive surface was 0·4 microlumen. The deflection was 5 divs. = 0·003 micro-ampère. This means an additional conductivity of 0·00015 micromhos, and a galvanometric efficiency of 375 micromhos per lumen.

Both these efficiencies are low, and as the sensitive surface is of about the same area as the pupil of the eye, this method evidently falls far short of the capability of the human eye in detecting a candle at 5 m.

Better results were obtained by charging a condenser through the selenium resistance and discharging it ballistically, but it was difficult to obtain consistent readings.

Electrometer Methods.

A Dolezalek quadrant electrometer giving 200 divisions per volt was used to measure the resistance of some high resistance selenium bridges, either by Cardew's method, or by inserting it in the galvanometer branch of a Wheatstone bridge. A change of 1/30th per cent. in the resistance was thus observed, due to an illumination of 0·001 lux. The galvanometric efficiency was of the order of 300 micromhos per lumen.

Results with Differential Galvanometer.

The best results, both as regards actual deflections and galvanometric efficiencies, were obtained with a Kelvin differential galvanometer having coils of a total resistance of 6280 ohms.

In order to be able to vary the illumination measurably within wide limits, the arrangement shown in the diagram (fig. 2) was adopted. The selenium bridge Se No. 3 was fixed on the bottom of the box B, which was optically blackened inside. At a distance of 25 cm. above the selenium was a circular opening 25 sq. cm. in area, closed by a plate of ground glass. A metallic filament lamp M was placed above the box at such a distance that the total candle-power of the ground-glass disc, as seen from the bottom of the box and determined photometrically, was 0·125. The illumination at the bottom of the box was thus 2 lux when the ground glass was lighted to give ⅛ candle-power. By placing a small diaphragm on the ground-glass surface, the illumination could be reduced to any desired amount. The faintest illumination so obtained was 10 microlux, or ten times that due to Arcturus unaided Since this was discovered by means of a selenium bridge, it means that it is possible to discover bright stars by means of selenium without the aid of any optical system whatever.

As ground glass does not necessarily give an illumination uniform over a wide angle, the precaution was adopted of picking out central, intermediate, and marginal portions of the ground glass in turn. Under the conditions here described no difference due to this shifting was discoverable, so that for the purposes of these measurements, as well as others described below, the ground glass may be considered as equivalent to a uniformly self-luminous surface.

One of the coils of the differential galvanometer K was put in circuit with a battery of accumulators, giving 80 volts, and the selenium bridge. The other coil, which had the same resistance, was traversed by a compensating current of the order of 6 micro-ampères.

A set of diaphragms was made by drilling round holes of different diameters in a piece of sheet copper. Complete series of measurements were made with four of these, called A, B, D, and E respectively. Two smaller ones, called F and G, gave somewhat uncertain results because the instrumental errors began to be comparable with the quantities to be measured.

The following table gives the diameters and areas of the apertures used, and the candle-power of the small circle of ground glass they exposed to the light, together with the illumination produced by that candle-power at the distance of the selenium bridge (25 cm.).

	Diameter.	Area.	Candle-power.	Illumination.
	cm.	cm.^{2}.	micro-candles.	microlux.
A	0·370	0·108	540·0	8640·0
B	0·305	0·0730	365·0	5840·0
D	0·207	0·0337	169·0	2704·0
E	0·107	0·0090	45·0	720·0
F	0·04	0·00126	6·3	100·8
G	0·025	0·00049	2·45	39·2

The galvanometer having been made nearly aperiodic, readings were taken after half a minute's exposure, then after half a minute's recovery, and so on alternately until successive "dark" and "light" readings had become sensibly constant. The exposures were made either by moving a light cardboard shutter or by switching on the lamp, the room being otherwise in complete darkness. Finally, the shutter having been closed, readings were taken for five or six half minutes in order to determine points on the "recovery" curve. The timing was done by listening to the beats of a metronome marking seconds.

The accompanying diagram (fig. 3) gives the readings so obtained in the case of aperture A.

On joining up the "light" and "dark" readings respectively, two curves are obtained whose vertical distance apart we may call the "amplitude" of the alternating exposure curve. These readings, therefore, give us two main results: the "total recovery" R, calculated as explained above, from two ordinates in the recovery curve; and the "amplitude" P. Both these quantities should be plotted against the illumination I, in order to discover the laws of the light action. This is done in fig. 4, which gives the total recoveries after various illuminations, and fig. 5, which gives the amplitudes for the same illuminations.

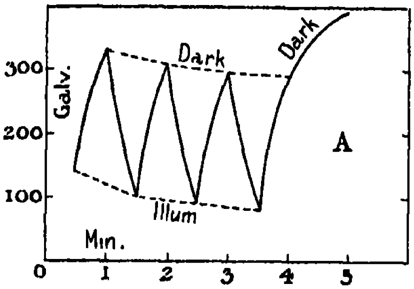

Fig. 3.

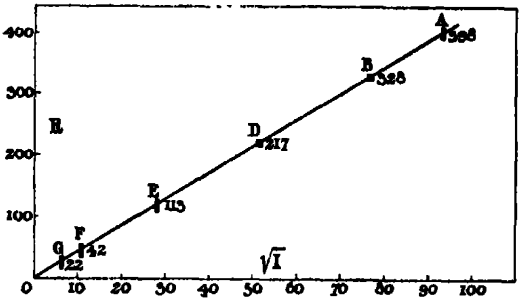

Fig. 4.

The values for the apertures F and G were too small to be obtained in the same way. They were somewhat roughly estimated by waiting until the deflection in the light seemed to approach a final value, then darkening and waiting until the recovery seemed to do the same, and taking the mean of the two deflections for the "total recovery."

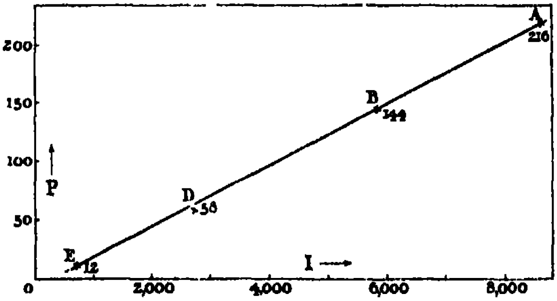

Fig. 5.

The following conclusions can be drawn from these curves:—

(*a*) The amplitude is proportional to the illumination. The curve is a straight line, which, however, does not pass through the origin, and probably has a curved portion between E and the origin (fig. 5).

(*b*) The total recovery is proportional to the square root of the illumination. This appears to hold rigidly down to the feeblest illuminations, as far as the limits of accuracy allow one to judge. These limits are indicated in the curve (fig. 4) by rectangles including all admissible values of the illumination and of the total recovery.

(*c*) The ratio of amplitude to total recovery is proportional to the square root of the illumination. This follows from (*a*) and (*b*), and is subject to the error specified under (*a*) for very faint illuminations.

One division (1 mm. at 1 m.) of the galvanometer scale represented a current of 0·00202 micro-ampère. This, with 80 volts, means that each millimetre of deflection indicates a gain or loss of conductivity amounting to 0·0000252 micromhos. Hence the "galvanometric efficiency" of the selenium bridge Se 3 is given by the following figures, which, of course show an efficiency inversely proportional to the square root of the illumination.

	Flux.	R.	Difference of conductivity.	Galvanometric efficiency.
	microlumen.	mm.	micromhos.	
A	0·864	398·0	0·010	11500
B	0·584	328·0	0·0083	14200
D	0·2704	217·5	0·00543	20100
E	0·0720	118·0	0 00285	39500
F	0·01008	41·0	0·001035	102000
G	0·00392	26·0	0·000655	167000

To discover still fainter illuminations, a minute hole, 0·013 cm. in diameter, was pricked in tinfoil, thus giving an illumination of 10 microlux (about that due to Venus unaided). It was not discoverable with certainty by means of bridge Se No. 3, but was easily discovered by means of a bridge of resistance 20,000 ohms, which could be worked with 15 volts. The "amplitude" was 11·1 divisions, derived from 20 alternate readings, during which, however, there was a strong drift owing to change of temperature. The efficiency is the same as in case of hole G.

Comparison with Potassium Photo-electric Cell.

It is of interest to compare the above results with the best performance of a potassium photo-electric photometer described by Elster and Geitel.* They placed a minute hole 0·038 sq. mm. in area in front of an amyl acetate lamp at 9·3 m. The illumination thus received was 3 microlux. The photo-electric current was then $6{\cdot}7 \times 10^{-14}$ ampère. With 10 microlux, in the last experiment, the current was 0·0222 micro-ampère. Selenium, therefore, with the same illumination and extent of sensitive surface, is capable of giving a measurable effect at least 100,000 times greater than that furnished by a potassium photo-electric cell.

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* J. Elster and H. Geitel, 'Phys. Zeitschr.,' 1912, vol. 13, pp. 468 and 739.

Comparison with the Human Eye.

The sixth magnitude is usually assumed as that of the faintest star clearly visible to the naked eye. Zöllner estimated the ratio of the brightness of the sun and Capella as 55,700,000,000. The sun's vertical illumination has been put at 50,000 lux (Exner). This would make the illumination due to Capella (magnitude 0·2) 0·9 microlux. A star of magnitude 5·2 would then give an illumination of 0·009 microlux, and an illumination one-third of that would have to be considered the limit of human vision. Let us call it 3 milli-microlux.

An attempt to test this limit experimentally was made as follows:—A 10-volt 1 candle-power electric lamp was encased in a cylinder closed with a disc of ground glass. To secure an even illumination of the latter, the cylinder was lined with white cardboard. An image of this disc was thrown by a lens on to another ground-glass screen G. The lens was stopped down by an iris diaphragm until the whole luminosity emitted by the screen G approached the limit of accurate comparison with a pentane lamp. At that point, the candle power of G, in the direction of the original beam produced, was found to be 0·00142, as compared with the pentane standard. The experiments were conducted in a dark room, and the eye was carefully protected from all stray light.

Further reductions were then made by inserting small measured stops into the iris diaphragm. When the area of the stop was 0·0007 sq. cm., the computed candle power of the illuminated surface of G, 5·7 sq. cm. in area, was 0·125 micro-candle. A faint "star" was then produced by placing a small stop on the ground glass G. A stop of area 0·0064 sq. cm. was not visible at all. A stop of area 0·0079 sq. cm. was visible after 10 minutes' accommodation to complete darkness, and a stop of area 0·0178 sq. cm. was clearly visible. Averted or "rod" vision was employed in every case as a final test. The object was 20 cm. from the eye. The candle powers were respectively 0·142, 0·175, and 0·395 milli-micro-candles. The illuminations at 20 cm. were 3·55, 4·36, and 9·9 milli-microlux respectively. Another observer obtained the same results, except that it was very difficult to perceive the second stop. On the whole, the results show a satisfactory agreement with the star estimates.

It was next attempted to find the limit of visibility of a faintly illuminated *surface*. The surface examined was the ground glass G, with the iris diaphragm stopped down by means of very minute holes pricked in tinfoil.

The results showed that a surface becomes invisible when its intrinsic brightness is less than 4×10^{-10} candles per square centimetre; 1 sq. cm. of the barely visible surface gives an illumination of 10 milli-microlux at 20 cm. If its brightness were concentrated at a point, that point would be clearly visible. The eye, therefore, suffers in sensitiveness when the light is diffused. The selenium detector does not. If the two were equally sensitive to a point source, the selenium detector would be more sensitive than the eye for faintly illuminated surfaces.

The fluxes of light discoverable by the eye are very minute. In the dark, the diameter of the pupil is about 6 mm., and its area 0·28 sq. cm. With an illumination of 3 milli-microlux, the flux received is $8{\cdot}5 \times 10^{-14}$ lumen. This is, therefore, the minimum flux of light perceptible to the eye.

The Theoretical Instrument Limit.

The limit reached with the experimental arrangements described above is still very far removed from the limit theoretically attainable with the most sensitive instruments now available. This is evident from the fact that a potassium photo-electric cell closely approaches the efficiency of the eye, although the current obtainable from it is 100,000 times feebler than the current furnished by the selenium bridge. Elster and Geitel worked with currents of the order of 10^{-14} ampère, which represents approximately the present-day limit of current measurement. Now if a current of the order of 10^{-9} ampère is obtained with an illumination of 10 microlux, a current of 10^{-14} ampère should, if the square-root law holds throughout, be obtainable with an illumination of 10^{-9} microlux, or the unaided illumination of a star of the 23rd magnitude, which is invisible in the most powerful telescope hitherto constructed. If, on the other hand, the current amplitude varies simply as the illumination, an illumination of 0·01 milli-microlux should be discoverable, which is at least 100 times less than that discoverable by the eye, so that stars of the 11th magnitude should show an electric effect unaided. This advantage over the eye would be kept whatever the optical system, so that a larger telescope would give no advantage to the eye without giving it to the selenium detector to the same extent. Selenium, therefore, offers an extension of our field of perception far beyond present optical or even photographic limits.

Bearing on the Theory of Quanta.

The efficiency of a lamp which converts the entire energy supplied to it into luminous radiation of the most visually advantageous type is 55 candles per watt. This value, given by Buisson and Fabry,* is intermediate between the values found by Drysdale and by Hyde, who obtained 17 and 72 respectively. That portion of the total flux of energy from a Hefner lamp which lies within the visible spectrum is about 200,000 ergs per second. The portion intercepted by 1 sq. cm. at 1 m. is 1·6 erg per second. This is the equivalent of 100 micro-lumen, and the illumination is 1 lux.

The eye, as we have seen, can perceive an incident luminous energy of $8{\cdot}5 \times 10^{-14}$ lumen, which is equivalent to 1360×10^{-12} ergs per second.

Planck's† energy quantum for a frequency n is $6{\cdot}55 \times 10^{-27} \times n$ erg. For a frequency $0{\cdot}58 \times 10^{-15}$, which is that of maximum visibility, the quantum is $3{\cdot}8 \times 10^{-12}$ erg.

The number of quanta received by the eye when receiving the minimum visible light is, therefore, about 360 per second. Any instrument, therefore, which has a sensitiveness 1000 or more times greater than that of the eye may be effective in discovering discontinuities in the light emission at feeble illuminations. As selenium is by far the most efficient detector known, the efforts in this direction made by N. Campbell‡ with Na-K alloy cells should be repeated with selenium bridges.

Effect of Invisible Radiations.

In comparing the efficiency of selenium with that of the eye or of other detectors, it is necessary to deduct the effect of the invisible spectrum. The maximum energy of most terrestrial sources of light is in the infra-red, and if selenium were, like the bolometer or the thermopile, simply a detector of radiant energy, its performances in detecting sources of terrestrial radiation could not be regarded as evidence of superiority in detecting visible radiations.

In order to study this question experimentally a new form of selenium bridge was constructed, consisting of a porcelain rod 0·25 cm. in diameter and 5 cm. long. Two thick parallel pencil lines were drawn lengthwise along the rod, leaving a clear white line 0·05 cm. wide and 4 cm. long between them. The white line was then bridged over with selenium, which was then sensitised. The result was a "line bridge" suitable for spectroscopic work. After constructing 12 such elements the most sensitive was chosen. It had a normal galvanometric efficiency of 250 micromhos per lumen.

This line bridge was exposed to the spectrum of a Nernst lamp produced by a 60° flint glass prism. The visible spectrum was 5·5 cm. long. That portion which affected the selenium was not longer than 8 cm. It was divided into half centimetres, and the line bridge was successively placed at each division. Half minute "amplitudes" were taken for each position, moving the bridge first from ultra-violet to infra-red and then in the opposite direction. The mean amplitudes so obtained for each position were divided into two groups, those for the invisible spectrum and those for the visible spectrum respectively. Expressed in percentages of the total radiation the effective energies were—

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* Buisson and Fabry, 'Comptes Rendus,' 1911, vol. 153, p. 254.

† M. Planck, 'Ann. der Phys.,' 1901, vol. 4, p. 553.

‡ N. Campbell, 'Camb. Phil. Soc. Proc.,' 1910, vol. 15, p. 513.

Ultra-violet	1·4
Visible	72·8
Infra-red	25·8
	100·0

Although it is evident that the invisible radiations are not in the aggregate as effective as the visible rays, the above figures do not necessarily represent the quantitative distribution of the effective energies. The latter cannot be accurately obtained without ascertaining the law of light action for each radiation separately.

This was done by Pfund* for short exposures and for two different intensities. He found a somewhat abrupt transition at a wave-length of 6500 Å.U. Below that wave-length the deflection was proportional to the square root of the energy, while from 7000 Å.U. to the end of the spectrum it was simply proportional to the energy. I have already mentioned that the deflections so obtained are not necessarily proportional to the total effect, and a more detailed investigation of the law of light action will be necessary for each part of the spectrum. Meanwhile, the following qualitative experiment shows that the dissymmetry found by Pfund does not apply to the final deflection.

The Nernst lamp spectrum was allowed to fall on a ground-glass screen closing the front end of a tube 43 cm. long, lined with white cardboard. Any portions of the spectrum could thus be recombined separately, and the selenium bridge at the other end received a definite portion of the aggregate energy of whatever parts of the spectrum were transmitted through the ground glass. The spectrum was divided into two portions which exerted equal actions. The division proved to be slightly on one side of the line C towards the blue. The separate effects were always in the aggregate greater than the total effect, showing that the effect varies as a power of the energy below the first power. The slit of the spectroscopic arrangement was then narrowed or widened, and the selenium exposed alternately to the two portions, as before. The intensity was thus varied in the ratio of at least 5 : 1, but the total deflections were sensibly equal for both portions. This shows that there is no great difference in the exponent of the energy for the two branches of the resonance curve.

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* A. H. Pfund, 'Phys. Rev.,' 1912, vol. 34, p. 370.

The general result for the spectral distribution of the effective energy is that about three-quarters of the total effect are due to visible radiations, even when the energy maximum is in the infra-red, as it is in most terrestrial sources. This proportion is maintained, or exceeded, with faint illuminations. If Pfund's relation held good, selenium would be sensible to none but those radiations which belong to the visible spectrum, if the light were faint enough. In any case, only some 30 per cent. at most need be deducted from the observed effect in selenium in order to reduce it to visible light.

The Detection of Small Changes of Brightness.

The limit of accuracy in photometric estimates is generally recognised to be ½ per cent., and as there is no optical means of increasing the contrast of two extended surfaces, a limitation is thus imposed upon the estimation of brightness such as physicists are not content to accept in other measurements. Contrast can be increased by photography almost indefinitely,* but it is a lengthy process, and gives no measure of the original contrast. It is therefore of interest to inquire whether selenium, besides being efficient as a detector of feeble light, is superior to the eye as regards the appreciation of minute differences of illumination.

To take a concrete case. A selenium bridge of efficiency 1000 will give 1000 micro-ampères with one volt if its surface is 1 sq. m. and the illumination 1 lux. With an illumination of 10,000 lux (feeble sunlight) the current will be 100,000 micro-ampères (assuming the square-root law), or 10 micro-ampères if the sensitive surface is only 1 sq. cm. A difference in the illumination amounting to 1 per cent. will make a difference of ½ per cent. in the current, or a difference of 0·05 micro-ampère (say, 100 divisions on the scale of a sensitive galvanometer). There is, then, no reason why a difference of 0·01 per cent. should not be electrically discovered, which, of course, is quite beyond the power of the eye.

This conclusion was confirmed by a number of experiments, one of which was the following :—

A ground-glass disc, 25 sq. cm. in area, was illuminated by a lamp from above. The disc then transmitted a light equivalent to 1/8 candle. A selenium bridge placed 25 cm. below the disc was exposed to this light, and was connected up to a P.O. resistance box. A battery of 8 volts and a Broca galvanometer adjusted to give 100 divisions per micro-ampère were also connected up. Adjustment being made for equilibrium, a black thread ¼ mm. thick was drawn across in contact with the ground glass surface. When passing across the centre of the disc it shaded off 0·6 per cent. of its area. A deflection of 8 divisions was obtained on the galvanometer. With 20 volts a deflection of 20 divisions was obtained. It was possible, then, to discover a variation of 0·03 per cent. with this comparatively insensitive arrangement. It is evident, therefore, that for such purposes as photometry and half-shadow polarimetry the selenium bridge must become a valuable accessory, capable of bringing these measurements up to the level of accuracy of other standard physical determinations.

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* E. E. Fournier d'Albe, 'Roy. Dub. Soc. Proc.,' 1909, 12, vol. 11, p. 97.

Summary.

1. The efficiency of selenium preparations used for detecting light is strictly defined, and standard conditions are chosen for determining it.

2. The efficiencies of some selenium preparations are evaluated from data given in previous publications.

3. Experiments are described which were made in order to detect minute quantities of light by means of selenium.

4. The minimum illumination reached is 10 microlux.

5. The law of light action is investigated, and shown to be, in the main, a square-root law, down to the feeblest illuminations.

6. The theoretical limit of light action discoverable by means of present-day methods and apparatus is calculated, and shown to be, with selenium, very far beyond the power of the eye.

7. It is shown that this offers a means of deciding the question of the discrete structure of radiant energy (theory of quanta).

8. It is shown, theoretically and experimentally, that selenium apparatus is capable of discriminating differences and variations of luminosity quite inappreciable to the eye.

Experiments on the Flow of Viscous Fluids through Orifices.

By G. F. Davidson, B.E. (Sydney), B.A. (Cantab.), 1851 Exhibition Research Scholar.

(Communicated by Prof. B. Hopkinson, F.R.S. Received May 23,—Read June 26, 1913.)

This paper deals with an experimental investigation of the flow of liquids through a round hole. In most of the experiments a fairly thick oil was used, and by varying its temperature the kinematic viscosity could be varied about a thousand-fold. It was possible by this means to change the character of the motion continuously from the type determined almost wholly by viscosity to the form in which the resistance was mainly due to inertia, and to follow the corresponding change in the relation of resistance and flow.

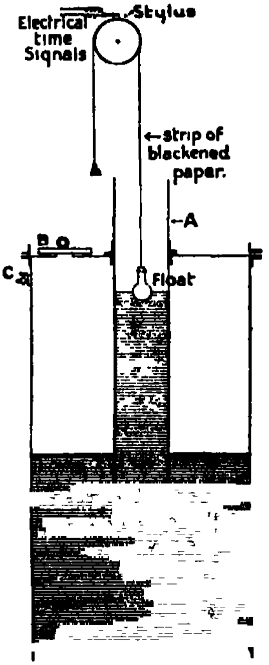

Fig. 1.

When the experiments were first undertaken it was hoped by comparing experiments with orifices of different sizes, and in which the viscosity and rate of flow were suitably varied, to obtain confirmation of the law of similar motion in viscous fluids. It was found, however, that this law did not hold, and the cause was discovered to be that the stress in this oil is not proportional to the rate of distortion.

Fig. 1 is a diagram of the apparatus used. The tube A was 20 cm. in diameter and 150 cm. long, closed at the bottom by a horizontal brass plate with an orifice at its centre. This tube was held in the centre of a tank 75 cm. in diameter and 150 cm. high. The tank was a closed vessel with a small cock C for admitting air under pressure and an aperture B, 10 cm. in diameter, by which the air pressure inside the tank could be suddenly released. The apparatus stood in a vertical position with the orifice immersed, say, 10 or 20 cm. below the surface of the fluid in the tank. Air pressure in the tank forced the fluid up in the tube A, so that the two surfaces of the fluid were about 100 cm. apart. On opening the aperture B the fluid in A flowed through the "drowned" orifice under a "falling head" until the two surfaces of the fluid came to the same level.

A float on the fluid inside the tube had a strip of paper attached to it which passed over a very freely running and evenly balanced aluminium wheel, and was held taut by a small weight attached to it. This strip of paper was blackened and passed underneath an electrically operated stylus which marked on it equal intervals of time (such as seconds for an orifice 2 cm. in diameter) as the level of the fluid fell in the tube A. The record was fixed with varnish, and from this the velocity of the surface of fluid in tube A can be found at any head, because zero head is marked on the paper at the end of each experiment when the fluid is at the same level inside and outside the tube.

Corrections in head are made for the variation in level of the fluid in the outer tank as the column of fluid inside the tube falls. Corrections in velocity are made for the velocity of approach. The correction required owing to the retardation of the falling column giving a greater head than the record showed was quite negligible.

Knowing the dimensions of the tube and the velocity it was possible to calculate the actual discharge. This divided by $\sqrt{(2gH)}$* × area of the orifice gives the coefficient of discharge, which we call C_d. Thus C_d can be plotted against head.

Actually, the records were measured up and two curves drawn, showing velocity and head each to a time base. Convenient readings of head were taken from these faired curves, and from the corresponding values the C_d was calculated so that the C_d against head curves do not show experimental errors. These errors were small, and the "fairing" of the original curves (to a time base) was almost unnecessary, the points being usually within 1 per cent. of the smooth curve.

Three orifices were used. They were 4, 2, and 0·5 cm. in diameter, and were made in plates 3·2, 1·6, and 0·4 mm. thick respectively. They were made geometrically similar by having the edge of the orifice rounded to a semicircle whose diameter was the thickness of the plate.

The fluid used was a heavy engine oil of good quality, with a flash point of 260° C. About 60 gallons were used in these experiments. It proved very suitable, and as it was kept in a closed vessel it remained perfectly clean and uniform during the 18 months it was under observation. It showed no signs of streakiness, although, of course, considerable care was needed to get such a large quantity at a uniform temperature when it was very viscous. In such cases it was "explored" with a resistance thermometer.

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* Where H is the difference in level of the two surfaces of the fluid at any instant and g is the acceleration due to gravity.

A wide range of viscosities was obtainable by varying the temperature. The value of μ/ρ was about 200 at 11° C., and 0·14 (about the same as for air) at 110°.*

The viscosity was measured by allowing 126 c.c. of the oil to flow under a small head through a tube 6·2 cm. long and 6·1 mm. in diameter. The viscometer was simply a spherical bulb with two tubes attached to it opposite one another, and held in a vertical position.

Errors were looked for both with water and oil, on account of wall effect, vortex motion, and baffling action by the bottom of the tank.

The wall effect was examined by putting sleeves of various diameters inside the large tube A, and observing when a variation in the coefficient of discharge due to this cause became perceptible. It was found to be negligible. The absence of vortex motion, that is the fluid swirling round so that a particle follows a spiral path towards the orifice, was proved by observing small floating bodies.

A baffle plate, distant only one diameter of the orifice away from it on the downstream side, had no effect on the C_d. Accordingly, the results are considered to be accurate within 1 per cent. for one infinite fluid flowing into another through this sort of round-edged orifice.

The working of the apparatus was tested with water flowing through sharp-edged orifices of 2 cm. and 4 cm. diameter. The results agreed well with those obtained by other experimenters.

It is interesting to note that with this arrangement it is possible to measure the C_d at much lower heads than in the case of an orifice discharging into air, because the surface of the fluid can be remote from the orifice, and is not affected by the motion there.

For water the C_d for a "drowned" orifice as compared with a "free" discharge is only reduced about 1 or 2 per cent.

A non-viscous fluid would have a constant C_d at all heads (somewhere about 0·7 for these orifices) until the pressures are such as to produce appreciable changes of density. The value which the C_d should have when flowing through an orifice in a thin plate into space has not been calculated for a circular orifice, although it has been for a long rectangular one.

Many experiments have been made to determine this C_d, which is in the neighbourhood of 0·6 for circular orifices with sharp edges.

With viscous fluids at low heads viscosity becomes relatively important, and the effect of inertia negligible. The velocity then is proportional to the head, and the curve C_d against head (H) should be a parabola, since C_d is really a measure of $V \div \sqrt{H}$.

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* Throughout the paper the word "viscosity" is used to signify the kinematic viscosity μ/ρ, denoted by ν.

Results for Oil.—Fig. 2 shows a set of curves of C_d against head for the orifice, 4 cm. in diameter.

The dotted lines for the curves at viscosities of 24·5, 49·7, and 206 C.G.S. units are the parabolas which the curve approximately follows under the low heads. That it does not do so completely is due to the fact that the viscosity of the oil is not independent of the rate of distortion, a point which is referred to later.

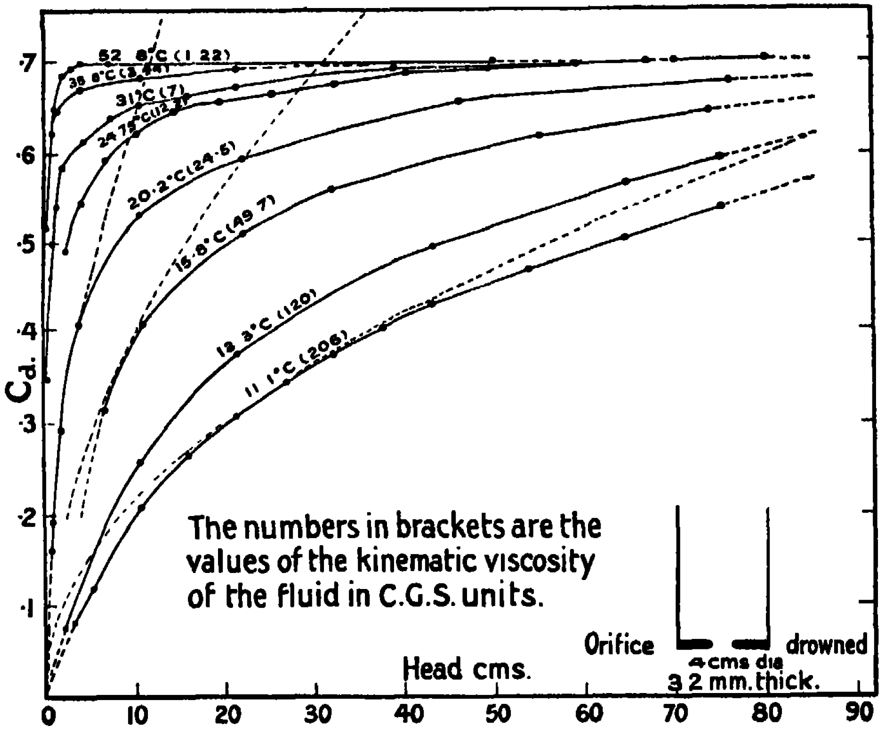

Fig. 2.

It is interesting to note the relative effects of the viscosity and inertia forces. Up to a C_d of, say, 0·3 the curve rises sharply, fulfilling more or less the parabolic law, but above this the inertia forces tend to flatten it until at a C_d of 0·65 the inertia effect is predominant, and the curve continues as an approximately straight line parallel to the H axis.

The general effect of viscosity is to turn the curves downwards.

Fig. 3, however, shows a curve for water, whose viscosity is about 0·01, which actually is curved in the opposite direction, and the flat part of its curve has a C_d below 0·66, while the viscous oils rise to 0·7.

On this figure also are shown three curves for fluids discharging through this round-edged orifice into air. It is interesting to note the small difference between the two curves for water. The two curves for oil discharging freely can also be compared with the corresponding ones for the drowned orifice, and it is to be observed that the difference becomes more marked as the viscous forces become more important.

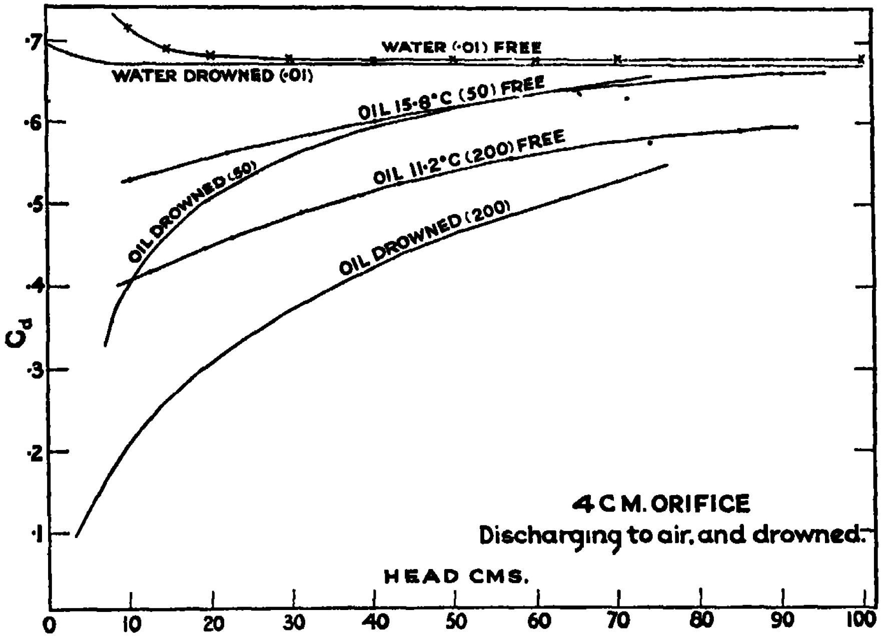

Fig. 3

One would expect the flat part of the C_d–H curve to attain the same value for all fluids. The curious thing is that, for a mobile fluid like water, flowing through a 4 cm. orifice, the flat part of the curve is considerably lower than that for the viscous oils. The water curve (even for the drowned orifice) also curves upwards, and at low velocities rises above the upper limit prescribed by inertia.

Another curious point is that at high heads with drowned orifices (as with air*) the curve is not truly flat, but varies slightly as the head increases.

These variations are probably caused by the viscous forces increasing the coefficient of contraction C_c, and decreasing the coefficient of velocity C_v.

For the coefficient of discharge, $C_d = C_v \times C_c$.

A viscous medium round the issuing jet, and the viscous resistance near the surface of the plate in the neighbourhood of the orifice, will both tend to increase the contracted area of the jet by giving the fluid a rotation outwards. In this way the C_c may be increased, while the inertia forces are so large as to keep C_v nearly unity.

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* Watson and Schofield, 'Proc. Inst. Mech. Eng.,' May, 1912.

Hence, at high velocities, the more viscous the fluid, the higher the flat part of the curve will be, as is shown by water and oil in these curves.

It is curious to find a friction effect like viscosity actually increasing the quantity discharged per second. At low heads with water, this same effect causes the C_d to rise above the value for the flat part of its curve, but, with a more viscous fluid, the C_v is so reduced that it overcomes the increase in C_c, and so the C_d is reduced and the curve is concave downwards.

It is of interest to apply to these results the principle of dynamical similarity.*

Consider the motion in an experiment in which the fluid has viscosity ν and the orifice is of diameter d. If the length scale of the motion be altered in the ratio L, and the velocity at every point multiplied by a constant V, a geometrically similar motion will be derived going through a similar orifice of diameter Ld. This second motion will in general be dynamically possible if, and only if, the viscosity of the fluid in which it occurs is $R\nu$, where VL/R is unity. Further, if this condition be fulfilled, the pressure at corresponding points, and, therefore, the heads under which these two motions go on, will be in the ratio V^2.

Conversely, if H be the head in the first case, then the similar motion so derived from it will be that which actually occurs when fluid of viscosity $R\nu$ flows through a tube of diameter Ld under a head V^2H. And if in any two experiments the head, the viscosity, and the diameter are so related that $d\sqrt{H}/\nu$ is the same for both, then the motions must be similar in these two cases, and the velocities at corresponding points, and, therefore, the average velocities which then hold, will be in the ratio of the square roots of the heads. Since C_d is equal to average velocity $\div\sqrt{(2gH)}$, it follows that it must be the same in both cases. That is, C_d should be the same in all cases for which VL/ν is the same, where V might be taken indifferently as representing the average velocity of the flow, or the square root of the head, L as the diameter, and ν as the kinematic viscosity.

In figs. 4 and 5 the values of C_d found in these experiments are plotted against VL/ν.

From these figures it is seen that C_d varies from 0·2 to 0·4 when $VL/\nu = 2$, from 0·4 to 0·6 when $VL/\nu = 10$, and so on.

The experimental errors are considered to be well within 5 per cent.

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* Dr. Stanton, 'Trans. Inst. Nav. Archs.,' March 22, 1912.

The variation of C_d in different experiments for which VL/ν is the same can only be explained by the failure of one or more of the assumptions underlying the application of the principles of dynamical similarity to fluid motion. These assumptions are: (1) That the stress varies as the rate of distortion.

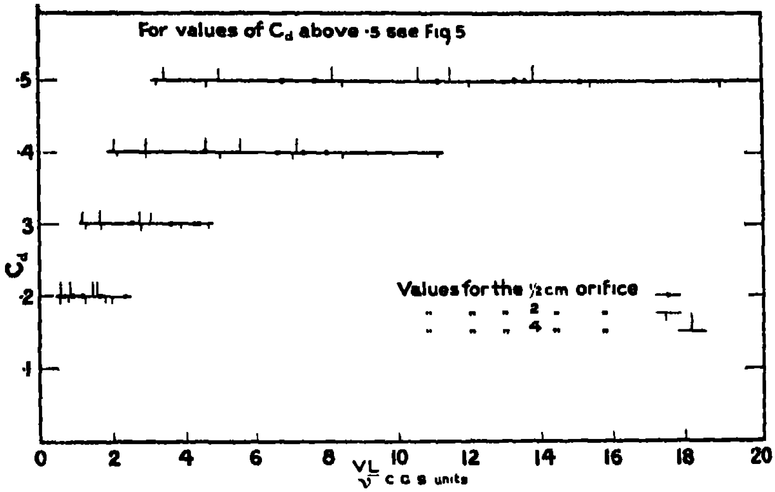


Fig. 4.

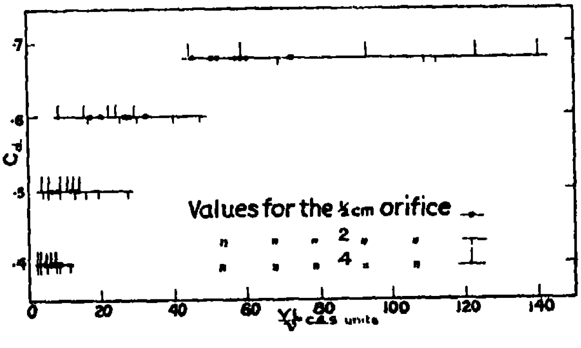


Fig. 5.

(2) That gravity does not determine the motion except in so far as it produces differences of pressure at points where the fluid is at rest.

That the second assumption is fulfilled in these experiments was proved by reversing the flow. The same results were obtained whether the flow was upwards or downwards through the orifice.

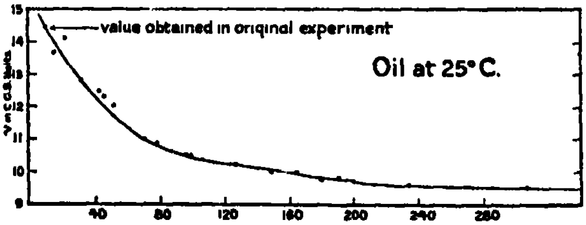
That the first assumption is not fulfilled for this oil is suggested by the divergence of the C_d-H curve (fig. 2) from the parabola, when the inertia forces are unimportant.

In order to determine the amount of variation of viscosity and its possible effects an absolute viscometer was made. It consisted of a glass tube 10¼ cm. long, and 2 mm. diameter, through which 220 c.c. of oil were caused to flow by air pressure. The air pressure came from a reservoir of 40,000 c.c. capacity, and was measured by a manometer. The volume of oil was measured in a spherical bulb of 220 c.c. capacity. There was one of these bulbs connected to each end of the capillary tube by about 4 cm. length of piping 1½ cm. internal diameter.

The viscometer was contained in a large water-bath to keep its temperature constant. The temperature was kept constant and the time of flow was measured. The head varied from under 4 cm. to over 52 cm. of mercury. The viscosity was calculated from the ordinary expression for flow in tubes and reduces in this case to ν = constant × time of efflux × head. The critical velocity (mean) would be about $\nu \times 10^5$ cm./sec. in this apparatus. Since the actual mean velocity never exceeded 15 cm./sec., and ν was over 9, there was no possibility of eddying motion. The apparatus was designed to give roughly the same average rates of distortion as occurred in the principal experiments with the orifices.

Owing to lack of time the variation of ν was only thoroughly examined at one temperature, namely 25° C. A few readings were taken at 35° C. (where ν is about 4) which showed the same sort of variation as those at 25° C., but not to such a marked extent.

The values of ν found varied from 13·7 to 9·4, and are shown on fig. 6 plotted against the rate of distortion, both being in C.G.S. units. The value of ν found in the first viscometer fits nicely on this curve.



Rate of Distortion (in secs.) = 8V/3 (Rad. of Tube).
Fig. 6.

The variation of viscosity with rate of distortion precludes any application of the laws of similar flow to these experiments, because the rate of distortion varies from point to point, and the corresponding changes in ν will alter the form of the flow. But generally speaking the effect of the changing viscosity is that the values of ν assumed in calculating the results exhibited graphically in figs. 4 and 5, are too high, the error being greater at the higher viscosities If allowance be made for this by taking in each case the value of ν corresponding to the actual average rate of distortion in that experiment, the result is to reduce somewhat the range of values of VL/ν corresponding to any given C_d. Thus the variation of viscosity may be said to furnish a qualitative explanation of the large divergences in this oil from the accepted laws governing similar motions.

It is perhaps worthy of notice that there were indications of a want of proportionality between stress and rate of strain in this oil even when it was as mobile as air.

This work was done at the Engineering Laboratory, Cambridge, and I wish to express my thanks to Prof. Hopkinson for his kind help and inspiring interest.

On the Electric Effect of Rotating a Magnetic Insulator in a Magnetic Field.

By Marjorie Wilson, B.A., M.Sc., and H. A. Wilson, D.Sc., F.R.S., Professor of Physics, Rice Institute, Houston, Texas, U.S.A.

(Received May 26,—Read June 19, 1913.)

In a previous paper[*] by one of us it was shown that when an insulator of specific inductive capacity K rotates in a magnetic field there is an electromotive force induced in it equal to that in a conductor multiplied by $1-K^{-1}$. The object of the experiments described below was to measure the induced electromotive force in a magnetic insulator rotating in a magnetic field parallel to the axis of rotation.

According to the theory based on the "principle of relativity" this induced electromotive force should be equal to that in a conductor multiplied by $1-(\mu K)^{-1}$, where μ is the magnetic permeability of the insulator, whereas on the theory of H. A. Lorentz and Larmor the appropriate multiplier appears to be $1-K^{-1}$, as for a non-magnetic insulator.[†]

No insulator is known for which μ differs appreciably from unity, so that it was necessary to construct a sort of model of a magnetic insulator. The insulator adopted consisted of wax, in which a large number of small steel spheres was embedded. The spheres were $\frac{1}{8}$ inch in diameter, and each one was coated thinly with sealing wax. The coated spheres were packed tightly and melted paraffin wax poured into the empty spaces between them so as to form a solid mass.

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[*] "On the Electric Effect of Rotating a Dielectric in a Magnetic Field," by H. A. Wilson, 'Phil. Trans.,' 1904. A, vol. 204.

[†] M. Abraham, 'Theorie der Elektrizität,' vol. 11, p. 322.

The insulator was in the form of a hollow cylinder with inside and outside metal coatings, and was rotated in a magnetic field parallel to the axis of the cylinder. The outside coating was connected to one pair of quadrants of a quadrant electrometer, the other quadrants of which were earthed. If an electromotive force E is induced in the cylinder and this raises the potential of the outer coating by V volts, then

$$E = V(C+C')/C,$$

where C is the capacity between the inner and outer coatings, and C′ the capacity of the electrometer connecting wire and outside surface of the outer coating. The inner coating is supposed earthed.

If the potential of the inner coating is raised by an amount E′, and this raises the potential of the outer coating by V′, then

$$E' = V'(C+C')/C.$$

Let the electrometer deflection due to V be d and that due to V′ be d'. Then we have

$$\frac{E}{E'} = \frac{V}{V'} = \frac{d}{d'}.$$

Thus E can be found in terms of d, d', and E′. Another way is to earth the outer coating and charge the inner one to a potential E′, then insulate the outer coating and afterwards earth the inner one. In this way a charge $-CE'$ is given to the outer coating which raises its potential to V′ and

$$-CE' = V'(C+C').$$

This second method has the disadvantage that it requires the outer coating to be earthed, so that errors may arise due to electric effects produced by opening the key connecting the outer coating to the earth. Also in the first method the potential E′ acts in exactly the same way as the induced electromotive force, so that errors due to bad insulation affect both V and V′ equally, and so are eliminated. The first method was therefore adopted. In the earlier experiments referred to above a small standard condenser was used to give a known charge to the outer coating, and the capacity of the cylinder was found in terms of that of the condenser. This method was less direct than that now employed.

The inner coating was connected to earth through a 10-ohm resistance which could be connected through a 90-ohm resistance to a dry cell. The potential difference between the ends of the 100 ohms was measured with a Weston voltmeter. When the cell was not connected the inner coating was earthed, and when it was connected the inner coating was raised to a potential one-tenth of that indicated by the voltmeter, which was usually 1·450 volts.

The apparatus was that used in the earlier investigation, with some improvements in detail. The cylinder was 3·73 cm. external diameter, 2 cm. internal diameter, and 9·5 cm. long. The outside surface of the cylinder was covered with a brass tube 0·6 mm. thick, and another brass tube fitted the inside surface. The inner tube was mounted on a shaft, from which it was insulated, and the shaft was mounted between fixed conical bearings and could be rotated by means of a belt driven by a ½-H.P. motor. The cylinder was surrounded by a large solenoid which produced a magnetic field parallel to the axis of rotation.

Two small brass wire brushes made contact, one on the middle of the outer coating and the other on the inner tube close to one end of the cylinder. The arrangement of the brushes is shown in fig. 1. Each brush was kept pressed down lightly but steadily by the weight of a brass bar fastened at right angles to the end of the rod supporting the brush as shown. The inertia of these bars prevented the brushes from jumping when the cylinder was

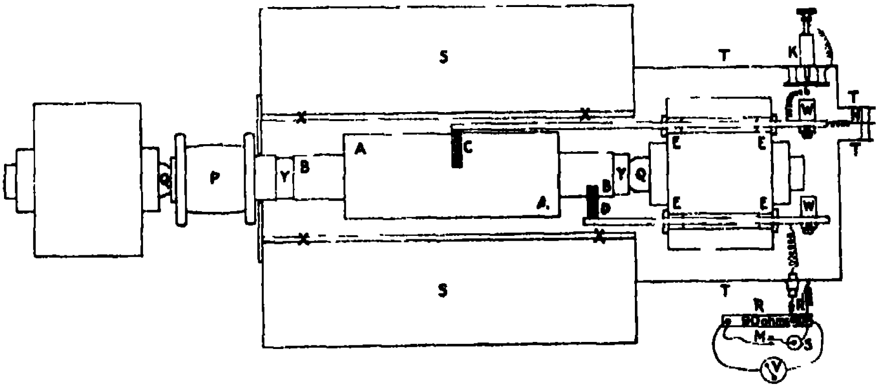

Fig. 1.

AA.	Outer coating of cylinder	WW.	Bars on brush rods.
BB.	Inner coating of cylinder.	K.	Key for earthing outer coating.
P.	Driving pulley.	TTTT.	Metallic screen.
SS.	Solenoid.	H.	Wire leading to electrometer.
C.	Brush on outer coating.	R, R'.	Resistances of 90 and 10 ohms.
D.	Brush on inner coating	M.	Key.
QQ.	Conical bearings.	S.	Dry cell.
XXXX.	Water jacket.	V.	Voltmeter.
EEEE.	Ebonite bushings supporting brush rods.	YY.	Fibre tube insulating BB from shaft.

rotating quickly and they could be adjusted so that the pressure on the brushes was very small. This new arrangement of the brushes caused a great improvement in the working of the apparatus. The electrometer and the wire leading to it were completely enclosed in a metal case which, with the solenoid, formed a complete electrostatic screen around the insulated system. The inside of the solenoid was kept cool by means of a water-jacket. The speed of the cylinder was found with a revolution counter driven by a worm gearing.

To make a determination of the induced electromotive force in the cylinder the electrometer deflection due to changing the potential of the inner coating by about 0·145 volt was first observed and then the cylinder started and its speed found. The effect of reversing a known current in the solenoid was next observed. The speed and sensibility were then again measured. The speed of the cylinder always remained constant within the limits of error. The sensibility also remained constant over long periods. The electrometer scale reading was very steady while the cylinder was rotating and the effect of reversing the current could be easily and exactly observed. In fact with the new arrangement of the brushes no difficulty in making the observations was experienced and the accuracy seemed to be limited only by the smallness of the deflections obtained. The cylinder insulated well.

There was no effect due to running the cylinder in the absence of a magnetic field and no effect due to reversing the current when the cylinder was at rest. The speed and sensibility were not changed by the current in the solenoid. The sensibility was the same when the cylinder was running as when it was at rest.

The following table contains a set of results obtained :—

Revolutions per second (n)	Electrometer sensibility (scale divisions per volt).	Current reversed in ampères. (c).	Deflection.	Effect in volts (E).	E/(nc).
99·0	184	7 5	5·63	0·0306	$4·16 \times 10^{-5}$
98·5	184	15 0	11·4	0·0620	4·20
98·5	184·5	10 0	7·6	0·0412	4·18
198·0	185	14·13	21·5	0·1160	4·14
				Mean	$4·17 \times 10^{-5}$

It will be seen that the induced electromotive force is very nearly proportional to the current reversed and to the number of revolutions per second. After these observations were made it was found that running the cylinder had produced a narrow air gap between the inner tube and the wax. This was filled up by slightly warming the cylinder and forcing down the mixture of wax and balls at the ends of the cylinder so that the mixture was very tightly pressed against the inner and outer tubes.

The best results could be obtained at about 100 revolutions per second. At greater speeds the electrometer reading was not always quite steady and at smaller speeds the deflections were too small. A set of six concordant measurements of the effect due to reversing about 14 ampères at 100 revolutions per second was therefore obtained and the mean of these was adopted as representing the result of the experiments. The mean results were as follows :—

Revolutions per second (n).	Electrometer sensibility.	Current reversed (c).	Deflection.	Induced E M F. (E).	$E/(nc)$.
104·0	250	14 34	15·4	0·0616	$4·13 \times 10^{-5}$

It will be seen that this result agrees closely with the others.

In order to compare the observed effect with that in a conductor, it is necessary to know the magnetic induction through the cylinder. Corrections for the induced electromotive forces in the metal coatings have also to be applied.

The change of average induction through the cylinder and its outer coating, due to reversing a current in the solenoid, was found by means of a spiral of fine wire wrapped round it uniformly from end to end. This spiral was connected to a ballistic galvanometer, and the secondary coil of an accurately known mutual induction was included in the circuit. The current in the primary of the mutual induction was measured with the same ammeter that was used to measure the current in the solenoid. The induction was found to be proportional to the current from 5 to 15 ampères, and to be equal to 4210 per ampère reversed. A second determination of this quantity was done, using a coil of two turns round the cylinder The induction through this coil was found for a series of equidistant positions along the cylinder and the mean induction through the cylinder calculated. The result was 4200. The mean of the two results, 4205, was adopted. The difference between the mean area of the windings and the area of cross-section of the cylinder was, of course, allowed for. The field at the windings was taken equal to that due to the solenoid in the absence of the cylinder.

The mean induction in the hole through the cylinder was found with a coil which could be slid along inside when the cylinder was supported in its usual position with the inner tube and shaft removed. This was found to be equal to 569 per ampère reversed. The field at the centre of the solenoid in the absence of the cylinder was found to be equal to 205 for a current of 2 ampères, which is the same as the value found in the earlier investigation done in the Cavendish Laboratory.

It was found that near the ends of the cylinder there was a stronger field than inside the hole through it. This, of course, was due to the magnetisation of the cylinder. In consequence of this there was an induced electromotive force in the inner tube which diminished the effect observed. The induction through the cross-section of the inner tube at the brush on it was found to be 740 per ampère reversed, so that the average potential of the inner tube was lowered by the electromotive force due to $740-569 = 171$ units of induction.

The induction through the outer cover was taken to be equal per unit cross-section to the field in the absence of the cylinder, which made it 143 per ampère reversed. An error in this quantity would have practically no effect on the final result for the ratio of the effect to that in a conductor, because it is to be subtracted from both quantities.

The induction through the cylinder at the brush on the outer cover was found to be 5010 per ampère reversed. This is greater than the average induction through the cylinder by $5010-4205 = 805$. In consequence of this the potential at the brush was raised above the average potential of the outside of the cylinder by the potential due to 805 units of induction per ampère reversed.

The observed effect, therefore, includes an induced electromotive force due to $805+143-171 = 777$ units of induction per ampère reversed, acting in the metal coatings of the cylinder. This gives $7{\cdot}77 \times 10^{-6}$ volt per ampère reversed per revolution per second. Subtracting this from the observed effect ($4{\cdot}13 \times 10^{-5}$) we get $3{\cdot}35 \times 10^{-5}$ volt per ampère reversed per revolution per second as the observed effect in the insulator itself.

The average induction through the insulator is $4205-(143+569) = 3493$ per ampère reversed. This would give an induced electromotive force in a conductor equal to $3{\cdot}493 \times 10^{-5}$ volt per ampère reversed per revolution per second. The ratio of the observed effect to that in a conductor is therefore

$$\frac{3{\cdot}35 \times 10^{-5}}{3{\cdot}493 \times 10^{-5}} = 0{\cdot}96.$$

The value of K for the insulator was found* to be 6·0 and that of μ to be 3·0, so that

$$1-(\mu K)^{-1} = 0{\cdot}944, \qquad 1-K^{-1} = 0{\cdot}83.$$

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* For method see earlier paper referred to above.

The accuracy of the value found for the ratio of the induced electromotive force in the insulator to that in a conductor depends on readings of the voltmeter and ammeter employed. The electromotive force was found in terms of the voltmeter reading, and the induction depends on the product of the mutual induction of the standard and the current determined by the ammeter. The primary of the mutual induction consisted of a single layer of wire wound in a screw thread of 1 mm. pitch cut on a brass tube 5 cm. in diameter and 90 cm. long. The screw was cut on an accurate lathe and the number of threads was found to be 10 per cm. to within 1 part in 5000. The secondary coil consisted of a single layer of 132 turns wound on an accurately turned brass cylinder, which fitted into the primary coil. The area of the secondary coil was known to within 1 part in 500. The mutual induction was therefore known to a higher order of accuracy than the other quantities involved. The voltmeter and ammeter readings only enter into the final result as the value of the ratio of the potential indicated by the voltmeter to the current indicated by the ammeter, because the same ammeter was used to measure the currents in the solenoid and in the primary of the mutual induction. The value of this ratio was found by means of a standard one-tenth ohm resistance. The following table gives the results obtained:—

Current through resistance by ammeter (C).	P D. between ends of resistance by voltmeter (E).	E/C.
5	0·500	0·1
9·95	0·995	0·1
15	1·500	0·1

The ratio E/C is constant and equal to the resistance of the standard, so that it seems certain that no appreciable error could have been introduced by the ammeter and voltmeter, which were new Weston standard instruments. It appears, therefore, that the induced electromotive force in the insulator agrees approximately with that to be expected on the theory of relativity. This theory involves no assumptions as to the constitution of the insulator, so that it is applicable to any medium having in bulk an average permeability μ and an average specific inductive capacity K.

The effect to be expected on the theory of H. A. Lorentz and Larmor depends on assumptions as to the constitution of the material medium so that it is doubtful whether their theory ought to be regarded as necessarily leading to $1-K^{-1}$ as the value of the ratio of the induced electromotive force in the composite medium employed to that in a conductor.

These experiments therefore confirm the theory of relativity but do not necessarily conflict with the fundamental assumptions of H. A. Lorentz and Larmor's theory. They do, however, make it probable that the application of this theory to magnetic bodies has not yet been worked out in a satisfactory manner.

[*Note added July* 16, 1913.—The specific inductive capacity and permeability of any material medium are average values over volumes large compared with the structural units (molecules or larger bodies) making up the medium. The medium employed has definite values of these quantities for volumes large compared with the volume of one of the spheres used in building it up. It appears, therefore, to be allowable to apply any theoretical results expressed in terms of μ and K to the medium used.]

Our thanks are due to the Government Grant Committee of the Royal Society for a grant with which a large part of the apparatus used in this investigation was originally purchased, and also to the Trustees of the Rice Institute for the facilities for experimental work which they have placed at our disposal.

On the Displacements of the Particles and their Paths in some Cases of Two-dimensional Motion of a Frictionless Liquid.

By W. B. Morton, M.A., Professor of Physics, Queen's University of Belfast.

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The paths described by the individual particles of a liquid have been investigated only in a few cases, excluding those in which the motion is steady, so that the particles follow the stream-lines. Clerk Maxwell,* in 1870, published drawings for the paths in an unbounded liquid disturbed by the passage of a circular cylinder. The curves for particles in contact with the cylinder were plotted by calculation; the other paths were drawn by eye from a knowledge of their terminal points and curvature. From these curves were derived others, showing the successive stages in the deformation of a row of particles which, before the approach of the cylinder, lay in a straight line perpendicular to its motion.

In 1885, Lord Kelvin† investigated the paths of particles of a liquid enclosed in a rotating ellipsoidal shell. He showed that they moved, relatively to the shell, along a set of similar ellipses in parallel planes, the period of this motion being the same for all the particles, so that after this period the configuration comes back to the initial one rotated through an angle.

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* 'Lond. Math. Soc. Proc.,' vol. 3; 'Collected Papers,' vol. 2, p. 208.

† 'Collected Papers,' vol. 4, p. 193.

Later (1889), Riecke[*] gave diagrams for the cases of translation of a sphere and of a vortex-pair. His method of procedure was the reverse of Maxwell's. He began with a straight row of particles, and, by giving them displacements proportional to the instantaneous values of their velocities, he obtained the approximate forms of the curves on which the particles lay from second to second. From these the curves described by individual particles were deduced.

Recently Havelock[†] has discussed some points of difficulty in the case of translation of a circular cylinder, specially with regard to the conditions at infinity. He has explained the uniform displacement forwards of the mass of the liquid. From a different point of view, that of meteorology, a problem of the same nature has been investigated by W. N. Shaw and Lempfert[‡] in tracing the paths of individual particles of air in the course of actual large atmospheric movements, supposed to be practically laminar, while the same problem, allowing for vertical movement of the air, has been more recently treated by v. Bjerknes.

In the present paper I have integrated the equations of motion and plotted curves for the paths of particles in the well-known simple cases of two-dimensional motion, viz., for liquid contained in a rotating elliptic cylinder and in a rotating equilateral triangular prism, and for liquid extending to infinity and disturbed by the translation or rotation of an elliptic cylinder.

The use of the word "particle" in this connection is convenient, but requires some explanation. What is really investigated is the motion of a mathematical point which moves at each instant with the velocity belonging to its position in the liquid. If at any stage a small sphere be put round this point and the motion of points on its surface be followed in the same way, it will often be found that the volume is continuously deformed as time goes on, being pulled out indefinitely in one direction. This happens, for example, in the simple case of irrotational circulation in a "free vortex." It occurs in liquid contained in a rotating triangular prism and in liquid outside a rotating elliptic cylinder. For liquid inside an elliptic cylinder, on the other hand, or more generally in Kelvin's case of an ellipsoidal shell, the "particles" are not continuously deformed, but come back periodically to their initial shapes. In this case the term particle can fitly be applied to a volume element throughout the motion; it is obviously inappropriate to the pulled-out filament.

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[*] 'Wied. Ann.,' vol. 36, p. 322.

[†] 'Univ. Durham Phil. Soc. Proc.,' 1911, vol. 4.

[‡] 'Life-History of Surface Air-Currents,' Publications of Meteorol. Office, 1906, No. 174, 1906.

This feature of the motion brings out the limitations inherent in the conception of the liquid as a continuum in the hydrodynamical treatment, and enforces our instinctive ideas of a molecular structure in actual liquids. This is pointed out by Havelock in connection with the deformation of volume elements in the immediate neighbourhood of a moving cylinder. The same point is illustrated in a still more striking way by the occurrence in many cases of points on the solid boundary where the relative velocity of liquid to boundary is zero. The "particle" at this point moves with the boundary, particles on either side approach it or recede from it continuously, remaining in contact with the wall. When there is approach from both sides toward this limiting position, the volume elements bounded on one side by the wall become extended indefinitely into filaments in the direction perpendicular to the wall.

General Summary of Results.

(i) *Elliptic Cylinder Rotating, Liquid Inside.*—Particles on the surface slide backwards along it, so that their excentric angles decrease by amounts proportional to the angle of rotation of the cylinder. Particles in the interior do the same thing along similar ellipses, so that the same row of particles constantly forms a radius vector of the ellipse. The paths in space are thus a family of similar looped curves (fig. 1). The apsidal angle and the width of the loops are found, and it is shown that consecutive loops intersect for ellipses less excentric than the form $b/a = 0{\cdot}64$ (fig. 2).

(ii) *Equilateral Triangular Prism Rotating, Liquid Inside.*—Particles on the walls move backward from one angular point to the other, and do not pass the corners. Their path has a single loop and has the circum-circle of the triangle as asymptote. Particles in the interior describe looped paths, the loops becoming closer and smaller towards the centre (fig. 3). Apsidal angle and width of loops are obtained (fig. 4).

(iii) *Elliptic Cylinder with Motion of Translation* through Liquid at Rest at Infinity.—The two particles on the surface which are carried in one piece with the cylinder, are those situated where the excentric angle is equal to the angle between the direction of motion and the major axis, and at the diametrically opposite point. These are the limiting positions between which the surface particles move in opposite directions round the two sides of the cylinder. The paths of these surface particles in space are looped curves extending from $-\infty$ to $+\infty$. Between the limiting points on each side of the ellipse there are two points at which the velocity of the particle in space has no component in the direction of motion of the cylinder, and one point at which the perpendicular component vanishes. Simple geometrical relations are found to connect these "stationary points" and the limiting points on the surface. For particles not in contact with the cylinder the paths are looped curves terminating at the initial position occupied by the particle before the approach of the cylinder and the final position where it is left when the cylinder has passed off to infinite distance. The line joining these end points is always parallel to the direction of motion of the cylinder and decreases rapidly in length at increasing distance from the line of motion. The direction of the path at its ends makes with the direction of motion of the cylinder an angle which is the same for all particles, and depends on the shape of the ellipse as well as on its direction of motion. The angle vanishes only for translation along a principal axis. In this case it is shown that for a given breadth of cylinder, and for particles lying beyond a certain distance from the central line, there is a definite shape of ellipse which is most effective in displacing the particle forward.

Diagrams are given for direct motion of four different forms of cylinder (figs. 5–8) and for oblique motion of a plane lamina (fig. 9). Also, for the deformation of a row of particles originally on a straight line (figs. 10–14).

(iv) *Rotating Elliptic Cylinder, Liquid Outside.*—As regards the configuration of the stream-lines relative to the ellipse, it is shown that there are two different cases according as the ellipse is more or less excentric than the form $b/a = \sqrt{2}-1$. For the less excentric forms the relative stream-lines completely surround the ellipse in all cases. In the other class there is a mound of liquid carried round by the cylinder at each end of the minor axis (fig. 15). Particles inside these regions describe closed paths relative to the cylinder and never escape from the neighbourhood of the minor axis. There is one particle in the centre of each region which moves in one piece with the cylinder, and four particles on the surface of the cylinder, at the boundaries of the "mounds," which do the same thing. These four points are limiting points at which the direction of motion of particles along the surface is reversed, and the circle passing through them is approached asymptotically by three different curves in space, viz., the paths of particles coming in opposite directions along the surface together with the path corresponding to the outer boundary of the "mound." The other paths in this case, and all the paths in the less excentric case, show recurring loops.

Diagrams are given for one ellipse of the less excentric kind (fig. 16), and for the plane lamina (fig. 17). Expressions are found for the apsidal angle of the paths which are examined in detail for the plane lamina (fig. 18). It is shown that for certain paths in the latter case there are three different apsidal distances.

Method of Calculation.

If ψ is the stream function for the motion of the liquid determined by the motion (u, v, ω) of a cylinder then the stream function for the motion relative to the cylinder is

$$\psi' = \psi - vx + uy - \tfrac{1}{2}\omega r^2.$$

The curves $\psi' =$ const. are the relative stream-lines.

The paths of the particles in space are got by combining a motion along these with the motion of the curves themselves as they are carried by the moving cylinder. Thus it is necessary to connect the position of a particle on its relative stream-line with the time or with the displacement of the cylinder from an initial position.

Let ψ' be expressed in terms of the appropriate orthogonal co-ordinates (ξ, η) with length-elements $d\xi/h_1, d\eta/h_2$, and let η be chosen to fix the position on a stream-line. The expression for the η-component of velocity gives the equation

$$\frac{d\eta}{dt} = h_1 h_2 \frac{d\psi'}{d\xi}.$$

When ξ is removed from the right-hand side by aid of the equation $\psi' =$ const., the integral can, in the cases considered, be expressed by elliptic functions.

ψ' will contain v or ω as a factor. It is convenient to replace dt as independent variable by $v\,dt = ds$ or $\omega\,dt = d\chi$.

The paths in space are got by applying to each point on a stream line the corresponding linear displacement s, or angular displacement χ.

(i) *Liquid Contained in a Rotating Elliptic Cylinder.*—

Here
$$\psi = \tfrac{1}{2}\omega(a^2-b^2)(x^2-y^2)/(a^2+b^2)$$
$$\psi' = -\omega(b^2x^2+a^2y^2)/(a^2+b^2).$$

The relative stream-lines are similar ellipses. Using the excentric angle η to fix position on one of them we find

$$d\eta/d\chi = -2ab/(a^2+b^2).$$

Thus in uniform rotation of the cylinder the particles slip back along their ellipses so that their excentric angles decrease at a uniform rate. This is a particular case of Kelvin's result for the ellipsoid. When the cylinder has turned through the angle $(a^2+b^2)\pi/ab$ the particles are back in their original relative positions. Each element of liquid has received a rigid body rotation through this angle in consequence of a motion which is differentially irrotational at each instant. Particles which at any instant lie on a radius of the ellipse continue to do so throughout the motion. Thus, it is easy to follow the progressive deformation and restoration of form of a small volume-element bounded by two radii and two elliptic arcs.

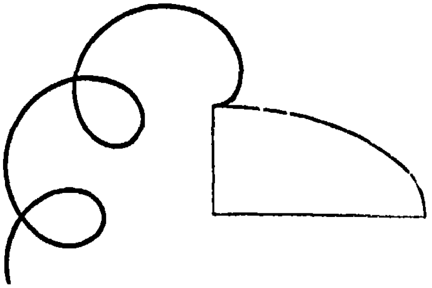

FIG. 1.

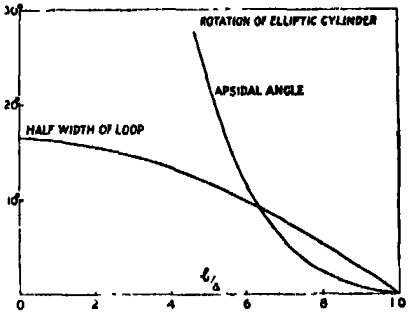

FIG. 2.

Fig. 1 shows the path of particles on the boundary of the ellipse in which $a = 2b$. For particles lying inside, the paths are similar curves. The apses of the path, of course, correspond to the ends of the axes of the ellipse; the motion is "direct" across the end of the major axis, "retrograde" across the minor axis. The stationary points occur when the particle is on the radius vector bisecting the angle between the axes.

The following results are easily obtained:—The apsidal angle of path is $(a-b)^2\pi/4ab$, so that the mean angular motion of the particles in space bears to the motion of the cylinder the ratio $(a-b)^2 : 2ab$.

The angular distance between the stationary points, *i.e.* angular width of the loops on the path, is $\frac{1}{2}\pi - \{(a^2+b^2)/ab\} \tan^{-1} b/a$.

In fig. 2 the apsidal angle and half-width of loop are plotted for different values of the axis ratio. The curves intersect near the value $b/a = 0{\cdot}64$, showing that for an ellipse of this shape successive loops are in contact. As the straight line limit is approached the width of a loop approaches a value of about 33°, while the apsidal angle becomes infinite.

(ii) *Liquid Contained in a Rotating Equilateral Triangular Prism.*—

Here
$$\psi = -\omega r^3 \cos 3\theta / 6a,$$
$$\psi' = -\omega(r^3 \cos 3\theta + 3ar^2)/6a,$$

where the side of the triangle is $a\sqrt{3}$.

The equation of the family of relative stream-lines

$$r^3 \cos 3\theta + 3ar^2 = b^3.$$

For $b^3 = 4a^3$ the curve breaks up into the sides of the triangle.

Using r as the coordinate-fixing position on the stream-line, we have

$$dr/dt = -\tfrac{1}{2}\omega r^2 \sin 3\theta,$$

giving

$$dr/d\chi = -(r^6 - 9a^2r^4 + 6ab^3r^2 - b^6)^{\frac{1}{2}}/2ar.$$

Let $\alpha^2 > \beta^2 > \gamma^2$ be the roots of the cubic in r^2, then the solution of this equation is

$$-\chi = 2a\,sn^{-1}\{(r^2-\gamma^2)^{\frac{1}{2}}/(\beta^2-\gamma^2)^{\frac{1}{2}}\}/(\alpha^2-\gamma^2)^{\frac{1}{2}}, \qquad \text{mod}\,(\beta^2-\gamma^2)^{\frac{1}{2}}/(\alpha^2-\gamma^2)^{\frac{1}{2}}.$$

β and γ are the apsidal distances on the stream-line, β being the radius drawn in direction $\theta = \pi/3$ towards an angular point of the triangle, γ that drawn towards the middle point of a side ($\theta = 0$). The third root $r = \alpha$ lies outside the limits of the triangle. The expression for χ vanishes when $r = \gamma$. It is convenient to identify a stream-line by the distance γ.

For particles in contact with the wall $\gamma = a$, then $\alpha = \beta = 2a$, the elliptic functions become hyperbolic and the integral takes the form

$$y = \sqrt{(r^2 - a^2)} = -a\sqrt{3}\tanh(\tfrac{1}{2}\chi\sqrt{3}),$$

where y is the distance from the middle point of a side. For $\chi = \pm\infty$ $y = \mp a\sqrt{3}$, *i.e.* the particles move backwards along the wall between one angular point and another, and do not pass the corners. The path of a particle in space then approaches asymptotically to the circumscribing circle of the triangle.

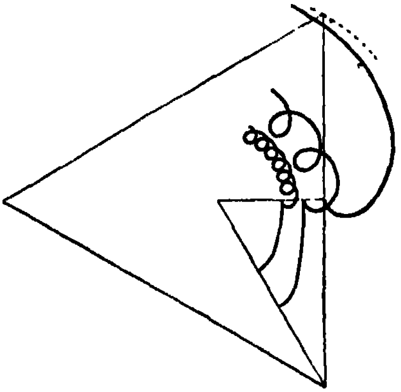

Fig. 3.

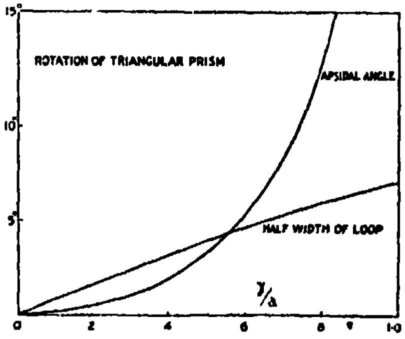

Fig. 4.

In fig. 3 the curves are drawn for $\gamma/a = 0{\cdot}6,\ 0{\cdot}8,\ 1$. A section of the relative stream-line is shown in each case, continued by the path in space.

The apsidal angle of the path is found to be

$$2a(\alpha^2 - \gamma^2)^{-\frac{1}{2}}\,\text{K} - \tfrac{1}{3}\pi.$$

The mean angular motion of the particle bears to the motion of the prism the ratio of this angle to $\frac{1}{3}\pi$.

The stationary points are determined by $d(\theta+\chi)/dr = 0$, which leads to $\cot 3\theta = 0$, $\theta = \frac{1}{6}\pi$, etc. So here, as in the last case, the radius to the stationary position bisects the angle between the apsidal distances.

The angular width of the loops as seen from the centre is

$$\tfrac{1}{3}\pi - 4a\,(\alpha^2+\gamma^2)^{-\frac{1}{2}}\,sn^{-1}\,\{\gamma^3/3a\,(\beta^2-\gamma^2)\}^{\frac{1}{2}}.$$

Fig. 4 shows how the apsidal angle and half-width of loop vary for stream-lines at different distances from the centre. It appears that successive loops come into contact when γ is about $0{\cdot}56a$.

(iii) *Translation of an Elliptic Cylinder.*—Let the velocity V make angle γ with the major axis, then, in terms of the usual elliptic co-ordinates,

$$\psi = \mathrm{V}ce^{-\xi+\alpha}(\cosh\alpha\sin\gamma\cos\eta - \sinh\alpha\cos\gamma\sin\eta),$$

where $\xi = \alpha$ on the surface of the cylinder.

Thus $$\psi' = \mathrm{V}ce^{\alpha}\sinh(\xi-\alpha)\sin(\eta-\gamma).$$

For the present purpose it is convenient to replace the co-ordinate η by $(\frac{1}{2}\pi+\eta-\gamma) = \eta'$, say, and to write the equation of the family of relative stream-lines in the form

$$\sinh(\xi-\alpha)\cos\eta' = \cot\delta.$$

Then η' is the argument and δ the modular angle of the elliptic functions which occur in the integral of the equation of motion.

The forms of these stream-lines are given in the text-books. It is easy to show that the line whose parameter is δ, at points very distant from the ellipse, runs parallel to the line of motion of the centre at a distance from this line of $(a+b)\cot\delta$. Particles which follow this particular stream-line will therefore have this for their initial and final distance from the line of motion of the centre. The passage of the cylinder results in all cases in a displacement of particles in the direction of its motion.* The motion along the relative stream-line is from $\eta' = \frac{1}{2}\pi$ when the cylinder is at infinite distance behind to $\eta' = -\frac{1}{2}\pi$ when it has passed off to infinite distance in front.

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* It seems clear that this will be the case no matter what is the form of the cylinder. The statement is equivalent to saying that in the steady flow of a liquid past a cylindrical obstacle each straight stream-line, after swerving round the obstacle, comes back to the prolongation of the same straight line. This appears physically obvious if we think of two of the stream-lines so far from the obstacle on opposite sides as to be practically straight throughout their length. The space between them, at great distances on the two sides of the obstacle, is filled across with straight intermediate lines of flow, so each of these lines, after deflection by the obstacle, must resume its former position.

The same argument does not apply to flow in three dimensions. If we consider a tube of lines of flow so far removed from the obstacle on all sides as to be straight, and take sections of it at great distances on both sides of the obstacle, the same bundle of tubes of flow comes out as goes in ; but there is now the possibility of the tubes having been twisted together in passing the obstacle, *e.g.*, if it possessed a helical structure.

The equation of motion in the original co-ordinate η is

$$d\eta/ds = 2e^{\alpha}\cosh(\xi-\alpha)\sin(\eta-\gamma)/c\,(\cosh 2\xi-\cos 2\eta),$$

where s is the distance the cylinder has moved from some fixed position.

Having obtained s from the integral of this as a function of η', the co-ordinates of successive positions occupied in space by the particle are found by applying the displacement s to the corresponding points on the stream-line. Let the origin be taken at the undisturbed initial position of the particle; let the axis of X be perpendicular to the direction of motion of the cylinder, and the axis of Y parallel to it. Then (X, Y), the sideways and forward displacements of the particle, are found to be given by

$$2\mathrm{X}\sin\delta/(a-b) = (e^{2\alpha}-\cos 2\gamma+\sin 2\gamma\tan\eta')/(\Delta\eta'-\cos\delta),$$

$$\begin{aligned}2\mathrm{Y}\sin\delta/(a-b) = (\cosh 2\alpha-\cos 2\gamma)\,\{\tfrac{1}{2}(3+\cos 2\delta)(\mathrm{K}-\mathrm{F}\eta')-2(\mathrm{E}-\mathrm{E}\eta')\}\\ -\{(c^{-2\alpha}-\cos 2\gamma)\tan\eta'+\sin 2\gamma\}\,(\Delta\eta'-\cos\delta).\end{aligned}$$

The special stream-line $\delta = \frac{1}{2}\pi$ includes the surface of the cylinder $\xi = \alpha$ and the hyperbola $\eta = \gamma$. The point $\eta = \gamma$ on the ellipse and the diametrically opposite point are limiting points for the motion of particles along the surface, *i.e.* points of zero relative velocity, as explained above. The paths of surface particles have, as asymptotes in opposite directions, the straight lines described by these points on the ellipse. The expressions for the co-ordinates X, Y become in this case

$$2\mathrm{X}/(a-b) = c^{2\alpha}\sin(\gamma-\eta)+\cos 2\gamma+\sin(\gamma+\eta)$$

$$\begin{aligned}2\mathrm{Y}/(a-b) = (\cosh 2\alpha-\cos 2\gamma)\log\tan\tfrac{1}{2}(\gamma-\eta)+c^{2\alpha}\cos(\gamma-\eta)+\sin 2\gamma\\ -\cos(\gamma+\eta),\end{aligned}$$

the origin now being at the point corresponding to $\eta = \gamma-\frac{1}{2}\pi$.

For the hyperbolic stream-line the co-ordinate ξ must be used. The values are

$$2\mathrm{X}/(a-b) = \sin 2\gamma c^{-(\xi-\alpha)},$$

$$2\mathrm{Y}/(a-b) = -(\cosh 2\alpha-\cos 2\gamma)\log\tanh\tfrac{1}{2}(\xi-\alpha)+(e^{\alpha}\cos 2\gamma-e^{-\alpha})\,e^{-\xi},$$

which vanish for $\xi = \infty$, and therefore give displacements from the initial position.

The following consequences can be deduced from the formulæ:—

(1) The distance between the initial and final positions of a particle is got by putting $\eta' = -\frac{1}{2}\pi$ in Y, which gives

$$(a^2\sin^2\gamma+b^2\cos^2\gamma)\operatorname{cosec}\delta\,\{(3+\cos 2\delta)\mathrm{K}-4\mathrm{E}\}/(a+b).$$

(2) The form of the paths at a great distance from the line of motion. When δ is small, X, Y, are small quantities of the same order, viz.,

$$X = \tfrac{1}{4}\delta\,(a-b)\sin(\eta-\gamma)\,\{e^{2\alpha}\sin(\eta-\gamma)-\sin(\eta+\gamma)\},$$

$$Y = \tfrac{1}{4}\delta\,(a-b)\sin(\eta-\gamma)\,\{\cos(\eta+\gamma)-e^{2\alpha}\cos(\eta-\gamma)\}.$$

Elimination of η gives the equation

$$X^2+Y^2 = \tfrac{1}{4}\delta\,(a-b)\,\{X\,(e^{2\alpha}-\cos 2\gamma)-Y\sin 2\gamma\}.$$

The paths, therefore, approximate to small circles, radius

$$\tfrac{1}{4}\delta\,(a^2\sin^2\gamma+b^2\cos^2\gamma)^{\frac{1}{2}}.$$

(3) Initial direction of motion of a particle. On differentiating the expressions for X, Y, and putting $\eta' = \frac{1}{2}\pi$, we get

$$dX/dY = \sin 2\gamma/(e^{2\alpha}-\cos 2\gamma),$$

which gives the tangent of the angle between the direction of motion of the cylinder and the direction in which a particle begins to move. It is the same for all the particles, and vanishes only when motion is along one of the principal axes. The greatest value is when $\tan\gamma = \sqrt{(b/a)}$.

For the case of a plane lamina, the angle in question is the complement of γ. So, if the lamina is moving at 45° to its plane, the direction of initial motion is parallel to the plane of the lamina. This is shown in fig. 9.

(4) The critical points on the surface of the cylinder. These are—

The limiting points, γ and $(\gamma-\pi)$, where the stream-lines divide;

The point γ', where the X-component of the velocity vanishes and the particle has its greatest sideways displacement;

The points η_1, η_2, on opposite sides of γ', where the Y-velocity vanishes.

The equation $dX/d\eta = 0$ with $\delta = \frac{1}{2}\pi$ gives

$$\tan\gamma\tan\gamma' = -b/a,$$

and $dY/d\eta = 0$ gives η_1, η_2 as roots of

$$\tan^2\eta+\{(a+b)^2\tan\gamma/a\,(a\tan^2\gamma-b)\}\tan\eta-b/a = 0,$$

so that
$$\tan\eta_1\tan\eta_2 = -b/a.$$

These equations show that γ, γ' and η_1, η_2 are pairs of conjugate points in the sense of Fagnano's theorem on the rectification of elliptic arcs. They have the same length of intercept on the tangent between the point of contact and the foot of the central perpendicular. Further, it is easy to show that if q be the length of this intercept for the pair (γ, γ') and q' for $(\eta_1\ \eta_2)$, the relation

$$q^2+q'^2 = (a-b)^2$$

exists between these, *i.e.* the sum of the squares of the intercepts is equal to the square of the maximum intercept at "Fagnano's point." The symmetry of this shows that the *rôles* of the two pairs of points can be interchanged.

(5) Influence of the shape of the ellipse on the displacements of a particle, the motion being along a principal axis.

Let the motion be along b, keep a constant, and let b increase, beginning with $b = 0$, for the transverse motion of a plane lamina.

If x_0 = undisturbed distance of a particle from the central line of motion,
X_0 = maximum displacement sideways, reached when the particle is on the a-axis,
Y_0 = final displacement in direction of motion,

then, in terms of the parameter δ,

$$x_0 = (a+b)\cot\delta,$$

$$X_0 = a(\operatorname{cosec}\delta - \cot\delta),$$

$$Y_0 = a^2 \operatorname{cosec}\delta\,\{(3+\cos 2\delta)\,K - 4E\}/(a+b).$$

The first and second equations show that, as b is increased, the same value of X_0 is found at distances from the central line proportional to $(a+b)$. So there is a continual increase of the sideways displacement of particles at given distance.

For the forward displacement we have

$$Y_0 = a^2 \operatorname{cosec}\delta \cot\delta\,\{(3+\cos 2\delta)\,K - 4E\}/x_0.$$

If the function of δ be plotted, it shows a maximum value about 74°, and closer calculation places this at 74° 15′. Therefore, to obtain the greatest forward displacement at distance x_0 we must have

$$(a+b) = x_0 \tan 74^\circ\, 15' = 3{\cdot}546 x_0.$$

This gives a positive value for b if $x_0 > 0{\cdot}282a$. For particles closer to the central line, the plane disc is the most effective form for causing forward displacement.

Description of Diagrams.—In fig. 5 I have drawn the paths of particles in liquid disturbed by the passage of a plane lamina. The motion must be supposed very slow and the edges of the lamina rounded, so as to avoid the occurrence of discontinuity. The direction of motion is perpendicular to its plane; the line with the arrow shows the path of the edge, the dotted line at the bottom gives the half-breadth of the lamina. The particles which are originally ranged along a line parallel to the plane of the lamina have positions relative to it defined by the values of δ = 80°, 70°, 60°, 50°, 40°, so that, if the half-breadth be taken as unity, their initial and final distances from the line of motion of the centre are given by the cotangents of these angles, say, 0·18, 0·36, 0·58, 0·84, and 1·19.

For comparison with this the following figures (6, 7, 8) show the paths of the same particles when the plane lamina is replaced by an elliptic cylinder of the same breadth, with axis b in the direction of motion of length $= \frac{1}{3}a$, a, and $3a$ respectively, as shown by the dotted quadrants. The values of b which would give maximum forward displacement to the five particles are 0, $0{\cdot}29a$, $1{\cdot}05a$, $1{\cdot}98a$, and $3{\cdot}23a$. In agreement with this it will be seen that

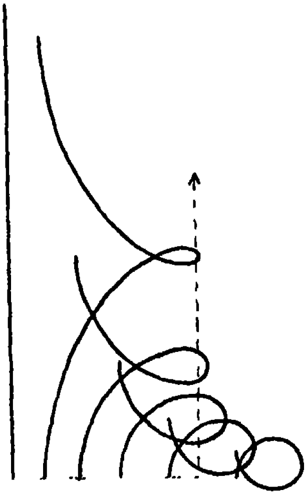

Fig. 5.

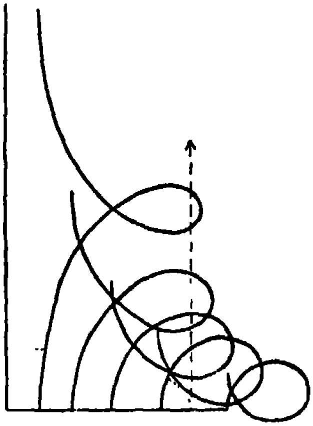

Fig. 6.

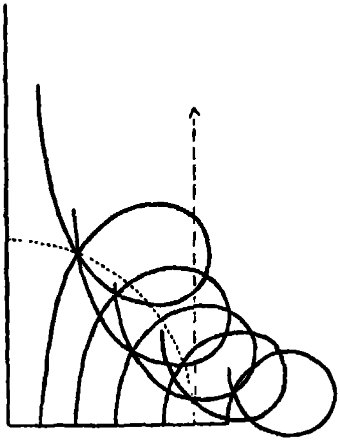

Fig. 7.

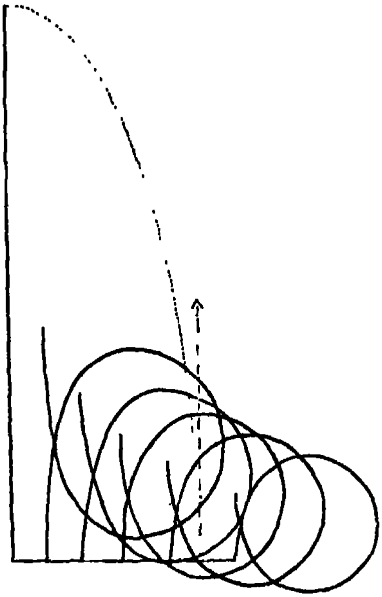

Fig. 8.

the first and second particles are displaced farthest in fig. 5, the third in fig. 7, and the fourth and fifth in fig. 8.

For particles in contact with the cylinder the paths extend to infinity in both directions, and have loops of the same type as the other curves shown. In the case of the plane lamina the loop contracts to a cusp. It did not seem worth while to reproduce these special curves.

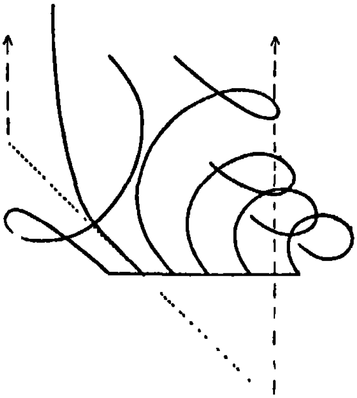

Fig. 9.

Fig. 9 shows the paths for a plane lamina moving at 45° with its plane. I have drawn a path, lying to the left of the central one, to show the symmetrical relation between corresponding paths on opposite sides of the line of motion of the centre of the lamina. It will be seen that one is got from the other by a double reflection. It has already been pointed out that this is the only case in which the directions of the paths at their ends are parallel to the moving plane.

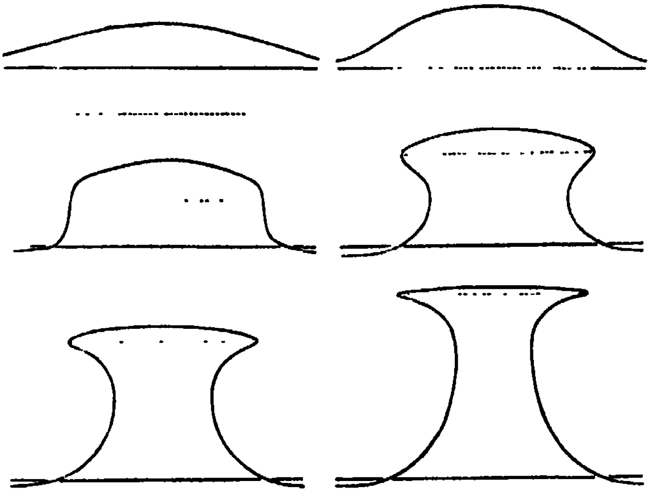

Fig. 10.

Figs. 10, 11, 12, show the successive forms assumed by a row of particles which, before the approach of the cylinder, lie on a straight line perpendicular to the direction of its motion. This initial position of the row is shown as a

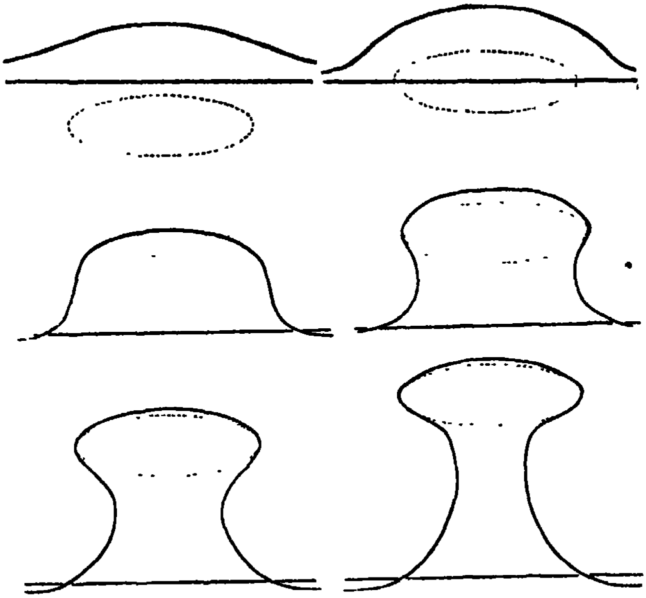

Fig. 11.

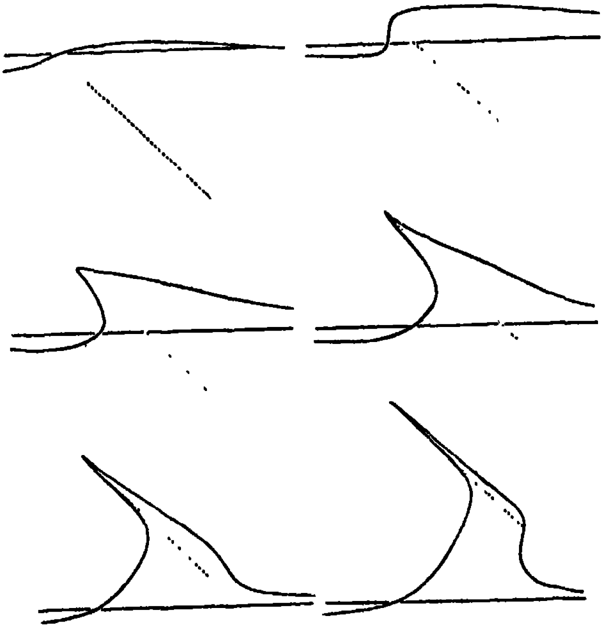

Fig. 12.

datum level in each figure; the position of the moving solid is shown dotted, the final configuration when the cylinder has moved off to infinite distance is the curve drawn through the upper ends of the paths shown on figs. 5, 6, and 9.

Figs. 13 and 14 give the forms of a row of particles lying originally on lines parallel to the motion of a plane lamina. The paths by which the particles have moved from their initial to their present positions are shown by dotted curves. Diagrams like these can be constructed by sliding a drawing of the relative stream-lines over another, giving the paths in space. This was the plan used by Maxwell. It has the practical drawback that the required points are given as the intersections of curves which are often nearly parallel to each other, so that a slight error in the setting, or in the forms of the curves, causes a large displacement of the intersections. I found it better to plot separately the co-ordinates X and Y against s, the distance travelled by the cylinder, and then to read off from these curves pairs of values for each s.

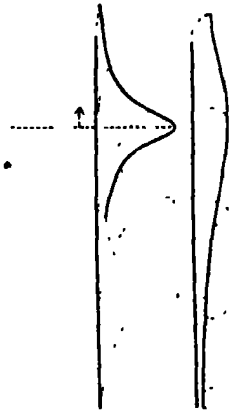

Fig. 13.

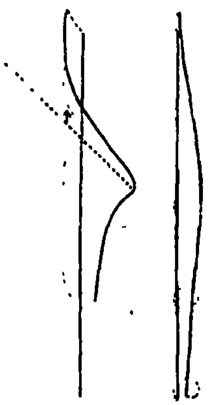

Fig. 14.

(iv) *Liquid Outside a Rotating Elliptic Cylinder.*—

$$\psi = \tfrac{1}{4}\omega c^2 e^{-2(\xi-\alpha)} \cos 2\eta,$$

$$\psi' = \tfrac{1}{4}\omega c^2 \{e^{-2(\xi-\alpha)} \cos 2\eta - \cosh 2\xi - \cos 2\eta\}.$$

The relative stream-lines $\psi' = \text{const.}$ show peculiarities which I have not seen any reference to, although the above expressions are very well known. The configuration of these curves is quite different for ellipses more excentric and less excentric than the critical form defined by $\sinh 2\alpha = 1$, or $a = (\sqrt{2}+1)\,b$.

Writing the equation of the family as

$$\cosh 2\xi + \{1 - e^{-2(\xi-\alpha)}\} \cos 2\eta = A,$$

the value $A = \cosh 2\alpha$ gives the surface of the ellipse. In the less excentric class this is the whole of the stream-line in question, but for the other class there is another part.

Solving the equation as a quadratic in $e^{2\xi}$

$$e^{2\xi} = A - \cos 2\eta \pm \{(A - \cos 2\eta)^2 + 2e^{2\alpha} \cos 2\eta - 1\}^{\frac{1}{2}},$$

with
$$A = \cosh 2\alpha.$$

$$e^{2\xi} = e^{2\alpha} \quad \text{or} \quad e^{-2\alpha} - 2\cos 2\eta.$$

The first value corresponds to the surface of the cylinder. The second is also admissible, provided the point defined by it lies outside the cylinder, *i.e.* if

$$e^{-2\alpha} - 2\cos 2\eta > e^{2\alpha} \quad \text{or} \quad -\cos 2\eta > \sinh 2\alpha.$$

If $\sinh 2\alpha < 1$, this gives a range of values of η extending downwards from the value $\pi/2$ on both sides. So there is an additional piece of the stream-line over the end of the minor axis and meeting the ellipse at the points defined by $\cos 2\eta = -\sinh 2\alpha$. These are evidently points of no relative motion.

The space between this additional piece of the stream-line $A = \cosh 2\alpha$ and the end of the minor axis is filled by closed stream-lines corresponding to smaller values of A. These contract to a point for $A = \sqrt{(e^{2\alpha} + 1)} - 1$; the position of this point on the axis is given by $e^{2\xi} = \sqrt{(e^{2\alpha} + 1)}$. Here also the particle of liquid remains in a fixed position relative to the rotating ellipse. All the liquid in the region occupied by the closed stream-lines is carried round with the cylinder, and is kept distinct from the remainder of the liquid. Stream-lines for which $A > \cosh 2\alpha$ encircle the ellipse. For the less excentric forms all the lines are of this type.

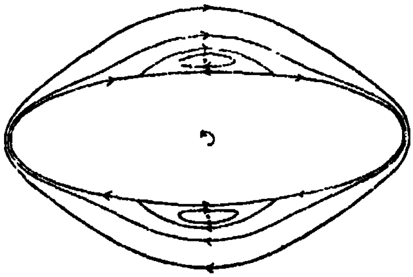

Fig. 15

The arrangement of stream-lines above described is shown on fig. 15 for $a = 3b$. Also, for the limiting form of the plane lamina, in one quadrant of fig. 17. The arrows show the direction of motion, as seen by an observer moving with the rotating cylinder. The less complicated forms for the less excentric class are shown on fig. 16 for $a = 2b$.

To find the paths in space the co-ordinate η is again used. Its connection with χ, the angle of rotation of the cylinder, is given by

$$d\eta/d\chi = -(\sinh 2\xi + me^{-2\xi}\cos 2\eta)/(\cosh 2\xi - \cos 2\eta),$$

where m is written for $e^{2\alpha} = (a+b)/(a-b)$.

The reduction of the integral, when the right-hand side has been expressed as a function of η, is rather tedious. The result is

$$\begin{aligned}\chi = &-\tfrac{1}{2}\eta + u\,\{3m+(\mathrm{A}m+2)p+\mathrm{A}p^2\}/2\,(2m+p)\,p^{\frac{1}{2}}(1-p^2)^{\frac{1}{2}}(m-\mathrm{A})^{\frac{1}{2}}\\ &+\tfrac{1}{4}(4m^2-1)^{-\frac{1}{2}}[\log\{(2m+1)^{\frac{1}{2}}\tan\eta-(2m-1)^{\frac{1}{2}}/(2m+1)^{\frac{1}{2}}\tan\eta+(2m-1)^{\frac{1}{2}}\}\\ &\qquad\qquad+\tfrac{1}{2}\log\{1+cn\,(w-u)/1+cn\,(w+u)\}+\Pi\,(u,\ w)]\\ &+\tfrac{3}{4}i\,[\tfrac{1}{2}\log\{1+cn\,(iv-u)/1+cn\,(iv+u)\}+\Pi\,(v,\,iv)].\end{aligned}$$

In this A is the stream-line constant, as above.

$$p = [\mathrm{A}^2-\{\mathrm{A}^4-4\,(m-\mathrm{A})^2\}^{\frac{1}{2}}]/2\,(m-\mathrm{A}),$$

$$cn\,u = -(p+\cos 2\eta)/(1+p\cos 2\eta), \qquad cn\,iv = 1/p,$$

$$cn\,w = (1+2mp)/(2m+p),$$

with $$k^2 = p\,(1-mp+\mathrm{A}p)/(m-\mathrm{A})\,(1-p^2).$$

These formulæ hold when $e^{2\alpha} > \mathrm{A} > \cosh 2\alpha$. When $\mathrm{A} > e^{2\alpha}$ the sign of the radical is changed in the definition of the constant p. When $\mathrm{A} < \cosh 2\alpha$ (in the more excentric class) k^2 becomes greater than unity and the reciprocal modulus is used. On the surface of the cylinder χ reduces to

$$\eta - e^{2\alpha}\tan^{-1}\{\tan\eta\,(\sinh 2\alpha-1)^{\frac{1}{2}}/(\sinh 2\alpha+1)^{\frac{1}{2}}\}/(\sinh^2 2\alpha-1)^{\frac{1}{2}}.$$

This for the class $\sinh 2\alpha > 1$. For $\sinh 2\alpha < 1$, $\tanh^{-1}$ replaces $\tan^{-1}$.

A good deal of labour is needed in order to get numerical values from the general formula.* The elliptic functions were taken from Legendre's tables. I took the amplitudes of modular angles to the nearest minute so that double interpolation was necessary. The Π functions were expressed by Θ functions and these were calculated from the expansions in ascending powers of "q." The values of q were got from the tables of Jahnke and Emde.

Apses on the Paths.—When the particles go right round the cylinder the apses are on the major and minor axes. The apsidal angle in space comes out

$$\begin{aligned}2\mathrm{K}\,[&\{3m+(\mathrm{A}m+2)p+\mathrm{A}p^2\}/2\,(2m+p)p^{\frac{1}{2}}(1-p^2)^{\frac{1}{2}}(m-\mathrm{A})^{\frac{1}{2}}\\ &\qquad+\tfrac{1}{4}(4m^2-1)^{-\frac{1}{2}}\Theta'(w)/\Theta(w)+\tfrac{3}{4}i\Theta'(iv)/\Theta(iv)]-\pi.\end{aligned}$$

The particles which keep near the end of the minor axis in the more excentric class, have apses in the two positions where they cross this axis. The apsidal angle is got from the expression just given by omitting the π

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* I am indebted to Miss Mary Bock for much help in the arithmetical work in connection with this case and the preceding one.

subtracted and replacing the denominator of the first term inside the bracket by $2(2m+p)p(1-mp-Ap)^{\frac{1}{2}}$.

Fig. 18 shows the variation of the apsidal angle for different values of the stream-line parameter A, in the case of a plane lamina.

For a certain range of the closed stream-lines there is a third apse intermediate between the two which correspond to the transits of the particle across the minor axis. This is where the particle is at maximum distance from the centre. We have

$$r^2 = \tfrac{1}{2}c^2(\cosh 2\xi + \cos 2\eta).$$

Differentiating with respect to ξ and taking account of the equation of the stream-line

$$dr^2/d\xi = -mc^2(\mathrm{A}e^{2\xi} - m \sinh 2\xi - 1)/(e^{2\xi} - m)^2,$$

which vanishes for

$$e^{2\xi} = \{1 + (1 - 2\mathrm{A}m + m^2)^{\frac{1}{2}}\}/(2\mathrm{A} - m).$$

For $\mathrm{A} = \cosh 2\alpha$ the maximum occurs at the point on the cylinder where the external part of the stream-line meets it. As A decreases the position of maximum r moves up the outer part of the stream-line until, for a certain value of A, it coincides with the more distant point on the axis. This happens when the value of $e^{2\xi}$ given above is equal to $(\mathrm{A}+1)+(\mathrm{A}^2+2\mathrm{A}-2m)^{\frac{1}{2}}$.

For the plane lamina $m = 1$ this gives $\mathrm{A} = 0{\cdot}84$. So the third apse is found on the paths between $\mathrm{A} = 1$ and $\mathrm{A} = 0{\cdot}84$. From $\mathrm{A} = 0{\cdot}84$ to $\mathrm{A} = 0{\cdot}732$, when the stream-line shrinks to a point, there are only the two apses corresponding to the positions on the minor axis.

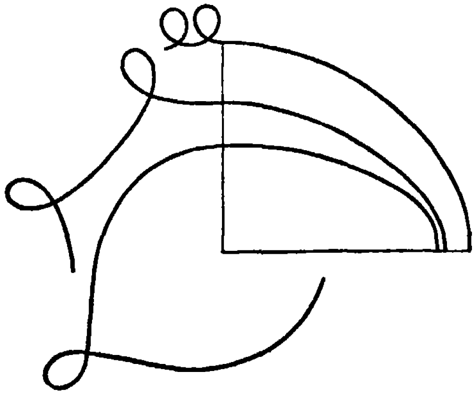

Fig. 16.

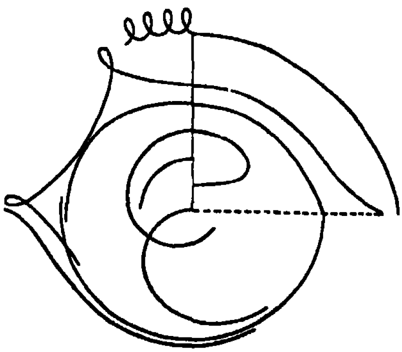

Fig. 17.

Description of Diagrams.—Fig. 16 shows the forms of the paths for an ellipse of the less excentric class $a = 2b$, $m = 3$. As in preceding diagrams the first quadrant is occupied by the relative stream-lines beginning with the surface of the cylinder itself A = $1\frac{5}{8}$. The two external lines are A = 2 and A = 3. These stream-lines are continued into the paths in space.

In fig. 17 the plane lamina is taken as the extreme case of the more excentric class. Here $m = 1$, and the surface of the lamina with the external loop corresponds to A = 1. The other stream-lines drawn are for the values A = 0·8, 1·2, 1·6. The paths are again shown as continuations of the relative stream-lines, except in the case of the outer portion of the lamina itself between the critical point $\eta = \frac{1}{4}\pi$ and the edge. The particles in contact with this move round the edge from the critical point on one side to that on the other side, the motion becoming infinitely slow near the limiting points. The path has a cusp at the edge of the lamina and approaches the asymptotic circle from the outside. It has been drawn, for the sake of clearness, from its cusp at the left-hand side of the diagram. It will be seen that the same asymptotic circle is approached from the inside by the path corresponding to the external loop and also by the particles which slide along the central part of the lamina between one critical position and the other.

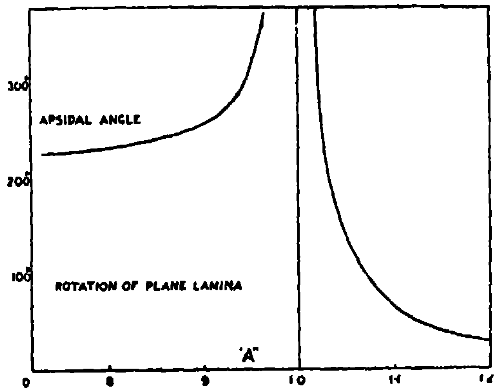

FIG. 18.

A Critical Study of Spectral Series. Part III.—*The Atomic Weight Term and its Import in the Constitution of Spectra.*

By W. M. Hicks, F.R.S.

(Received June 7,—Read June 26, 1913.)

(Abstract.)

The wave numbers of the lines in a spectrum which form any of the recognised series can be calculated, as is well known, from an expression of the form

$$n = \frac{N}{D_1^2} - \frac{N}{D_m^2},^*$$

where $N = 109675$ and $D_m = m +$ fraction, the fraction being in general a function of the integer m. The constant doublet or triplet separations of S and D series are formed by the deduction of a quantity Δ, or Δ_1, Δ_2, in the case of triplets, from D_1, and it has long been known that these quantities are very roughly proportional to the squares of the atomic weights when elements in the same group are compared. The present communication deals with the actual relation between Δ and the atomic weight, and with the part it plays in the general constitution of spectra.

It is shown that there is a definite quantity in connection with each element which is of fundamental importance in the building up of its spectrum. It is proportional to the square of the atomic weight: in fact, if w denote the atomic weight divided by 100 its value is $(90{\cdot}4725 \pm 0{\cdot}013)w^2$. This quantity is of such universal application that it is useful to have a special name for it, and it has been called the oun (ὠν). Its value is denoted by δ_1, but δ is used for the multiple $4\delta_1$, as it is of very frequent occurrence. The evidence for its existence is based on the arc spectra of He, the elements of the Groups I and II, the Al sub-group and Sc of III and the O, S, Se of VI of the Periodic Table—in other words, all those elements in which the series lines have been allocated. It is found :—

(1) That the Δ which give the doublet and triplet separations are all multiples of their respective ouns.

(2) That the corresponding quantities, which give the satellite separations in the D series, are also multiples of the oun.

(3) That the F series show satellites depending in a similar way on the oun.

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* It will be convenient to refer to N/D_m^2 as $V(n)$ and N/D_1^2 as $n(\infty)$.

(4) That, in a large number of cases, lines are related in such a way that the differences of their denominators are multiples of the oun, and that frequently in place of an expected line which is not observed another occurs related to it in this manner. It is said to be collaterally displaced.

After reviewing the evidence for the existence of the oun the paper deals in succession with:—

(*a*) The constitution of the D series. After establishing the dependence of the satellite separations on the oun, it is shown to be possible that the D series may not depend directly on a formula involving *m*, but that the D_m of different orders may be given by the successive addition, or subtraction, of various multiples of the oun. It is curious that in those cases where there are no satellites, these differences are multiples of the Δ themselves. Evidence is also given to show that the decimal part of D (2), *i.e.* for the first line, is a multiple of Δ, or Δ_2 for triplets, but that, in the case where satellites exist, the extreme satellite is to be taken.

(*b*) The constitution of the F series. The F series is one whose limit is the variable part in the formula for the D series corresponding to the first of the D lines; in other words, it depends on the D series in the same way that the limits for the S and D series depend on the first line of the P. For all elements, except the alkaline earths, the lines are far in the ultra-red, and it is only recently that waves of extreme wave-lengths have been measured by Paschen. It is probable that the VF for the first lines in each sub-group may be the same, and even possible that it may be the same in all, the earths excepted. In the earths there are a very large number of strong well-defined lines which are connected collaterally with one another, or with the lines of the series themselves, the displacements proceeding by multiples of Δ. These afford values of large multiples of Δ, and hence of δ; and, in consequence, give very exact values for the latter.

(*c*) The preceding results are then discussed with a view to obtaining a better approximation to the value of the oun as a function of w^2, on the supposition that it is always proportional to it. A value is obtained (see above) which is probably correct to a few units in the fifth significant figure. With further knowledge it is probable that this degree of accuracy may be extended to the sixth, and even beyond. It is clear that with such a knowledge of this constant, and with more definite and certain knowledge of spectral relations enabling values of δ of the same degree of accuracy to be obtained, it will be possible to determine atomic weights with extreme accuracy, an accuracy much beyond that attainable by methods depending on weighing.

The large atomic weight of Ag, combined with the fact that it may be regarded as the basis of other atomic weights, would point to it as the best single element from which to deduce the value of δ/w^2. The value of its doublet separation can be determined with extreme accuracy, to one or two units in the sixth significant figure. But, unfortunately, the deduction of Δ from this is subject to an uncertainty which quite upsets that degree of accuracy. The most probable value is, however, very close to that obtained by the final discussion. The uncertainty is due to a doubt as to the real relations of lines usually assigned to the S, D, and P series in Ag, and it is hoped to clear this up by a further consideration of the spectrum. It is then shown how the laws indicated in the foregoing discussion enable the doublet and the satellite differences for Au, and the limits of the series to be determined.

The value of Δ for Sc is considered in Appendix I. In Appendix II, the wave-lengths of the D and F lines treated of, together with short historical notes, are given.

A Band Spectrum attributed to Carbon Monosulphide.

By L. C. Martin, A.R.C.Sc., B.Sc., Research Student Imperial College of Science and Technology, South Kensington.

(Communicated by A. Fowler, F.R.S. Received June 10,—Read June 26, 1913.)

[Plate 6.]

The experiments described in the present paper were made in connection with the investigation of sulphur spectra developed by the nitrogen afterglow, in continuation of previous observations by Profs. Strutt and Fowler.*

A result of considerable interest is the detection of a series of ultra-violet bands which appear to be characteristic of a compound of sulphur and carbon. This band system extends from λ 2436-2837 approximately. It is, however, quite distinct from that developed, in the same region, by carbon disulphide in the afterglow, which is described in the paper to which the reference is given. Further photographs were taken, and it was found that the two sets of bands had nothing whatever in common.

Confirmation of Prof. Strutt's work on the chemical actions taking place between carbon disulphide and the active nitrogen was obtained. A green deposit of nitrogen sulphide formed in the experimental tube, and also a brown one of polymerised carbon monosulphide, the latter only in the presence of a stray discharge.

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* 'Roy. Soc. Proc.,' 1911, A, vol. 86, p. 111.

Sulphur in the Carbon Arc.

The new bands were first observed in an attempt to obtain the spectrum of sulphur in the carbon arc. After some failures, successful results were obtained by using a hollow carbon, well charged with sulphur, as the upper pole, which was made positive. In these circumstances a steady flow of melted sulphur into the arc was maintained.

In addition to overpoweringly strong bands of carbon and cyanogen, and faint bands recognised as belonging to sulphur, several of the photographs showed a fairly well developed system of bands in the region 2500–2700 of which no previous record could be found. Like the sulphur bands, the new bands were degraded towards the less refrangible side.

Attempts to brighten the spectrum by surrounding the arc with sulphur vapour from a test-tube in which sulphur was boiled by a bunsen burner increased the intensity of this set of bands, but brought out a good many *reversed* sulphur bands in the region 2800 to red. The band system 2500–2700 betrayed no tendency to reversal. It therefore seemed probable that these bands were not due to sulphur itself, but to some compound produced in the arc.

Sulphur Vacuum Tube.

As a check on the previous result, experiments were made on the electric discharge through sulphur vapour. Salet's apparatus* is very suitable for the visible region of the spectrum, but fails for short wave-lengths, since it is generally constructed of glass, and would be difficult to make of silica glass.

An arrangement was accordingly devised (fig. 1) with a quartz window (Q). The sulphur could be melted in side tube (A) by means of gentle heating with a bunsen burner. The electrodes (B) were of aluminium, led into the discharge tube by quill tubing within the wider side tubes, and cemented in with sealing wax. With apparatus of the dimensions shown, it was found that the quartz window was hardly at all clouded during the 15 minutes necessary for exposure. The tube was first exhausted with a pump and the vacuum was subsequently maintained by means of charcoal cooled with liquid air (see D, fig. 1). The discharge, as described by Salet, is of a blue colour, and is luminous enough, even in the fairly wide tube, to require only a short exposure.

In the first experiments, with a less perfect form of apparatus, giving an insufficient supply of sulphur vapour, the characteristic sulphur bands were accompanied by bands of nitrogen and the lines of carbon and mercury at 2478, 2536, respectively. The new system of bands in the region 2500–2700 was also faintly present.

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* G. Salet, 'Analyse Spectrale,' p. 220.

When the more perfect apparatus was employed, however, nitrogen, carbon, and mercury were eliminated and the new bands were also absent; the spectrum then only extended as far as 2829 into the ultra-violet and showed nothing but the broad, double-headed sulphur bands degraded towards the red. It is clear that these bands 2500–2700 are not given by the discharge through pure sulphur vapour; also that they are only developed to any strength when the carbon line 2478 is present. They have nothing whatever to do with the ordinary spectra of carbon or nitrogen.

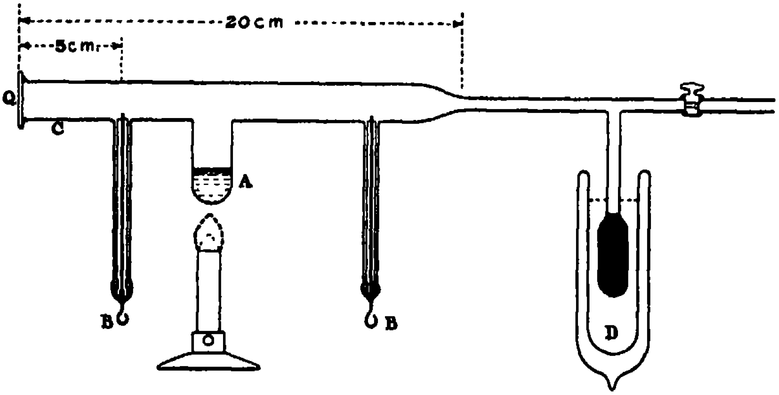


FIG. 1.

Discharge in Carbon Disulphide.

The spectrum of the electric discharge through the vapour of carbon disulphide was next photographed. A similar apparatus to the previous one was used, the carbon disulphide being contained in a bulb, and the flow of the vapour was regulated by a tap. The vapour was led into the tube at C (fig. 1). As in the previous case it was easy to maintain a good vacuum by means of charcoal and liquid air, especially as in this case the action of the discharge tends to decompose the vapour and lower the pressure still further.

The discharge from a 10-inch coil immediately gave a heavy dark brown deposit on the walls of the tube, doubtless being a mixture of sulphur and polymerised carbon monosulphide as described by Dewar and others. This deposit extended to the liquid-air tube. It was found that by lengthening the discharge tube slightly, the quartz window could be kept free from deposit.

The spectrum was found to be very complicated. In the first place it reproduces that of the sulphur vacuum tube perfectly, band for band, and it seems probable that this is due to free sulphur, one of the immediate products of the discharge.

Corresponding in intensity to the sulphur bands is a remarkable band system extending from λ 2436–2837, the brightest of the bands being identical with those previously shown by sulphur in the carbon arc.

Discharge in Disulphur Dichloride.

It was thought desirable to test whether or not these bands were due to sulphur in a different molecular condition from ordinary sulphur vapour, and for this purpose an unstable and volatile sulphur compound was necessary; such a compound is disulphur dichloride. An apparatus similar to that adopted for the carbon disulphide discharge was used, and was kept exhausted by means of cooled charcoal. The defect in this apparatus was that the bulb containing the disulphur dichloride was connected to the discharge tube by means of a short piece of thick red rubber tubing such as is used for vacuum tube work. The discharge produced a blue glow as in the two previous cases and a deposit was immediately formed on the walls of the tube, found on after examination to consist of sulphur and a higher chloride. The spectrum of the discharge contained the usual sulphur bands and faint indications of the new bands. The carbon line 2478 was present and the impurity was found to be due to the action of the disulphur dichloride on the rubber connection. To make certain of this another tube was constructed and the bulb sealed on; it could be filled with the liquid by a fine bent tube on removing the tap stopper.

On taking a photograph with an even longer exposure than before, the carbon line and the new bands were found to be eliminated, the sulphur spectrum only being left in its entirety.

Description and Wave-lengths of the New Bands.

As already explained, when fully developed, the new spectrum consists of a number of bands degraded to the less refrangible side. With the spectrograph employed, giving a dispersion of about 10 Å.U. to the millimetre in this region, a few of the bands were just resolved into their component lines. Like the sulphur bands they appear fairly evenly spaced and double headed, and like those of the carbon arc they form groups in which successive heads diminish in intensity, although in the opposite direction to the carbon bands, which are degraded towards the violet.

The group with its head at 2579 is worthy of special mention. Its appearance varies greatly under different conditions, and it appears to be the best developed of all the bands only when the whole system is weak. It is the strongest in the carbon arc spectrum of sulphur, and in cases where sulphur vapour is contaminated with carbon in the vacuum tube. In the carbon disulphide discharge, however, where the whole of the bands are strongly shown, it is not so bright relatively, and is evidently superposed on another group with a fairly strong band near 2573. In this case the head at 2665 is the brightest of the system.

The wave-lengths of the bands were determined as accurately as possible by means of an iron comparison spectrum in the usual way. Except in the extreme ultra-violet, where the resolving power is high, the heads of the bands were very diffuse and indistinct, and consequently very difficult to measure. As the second-frequency differences are small it has not been at present found possible to give a Deslandre's frequency formula for the band system.

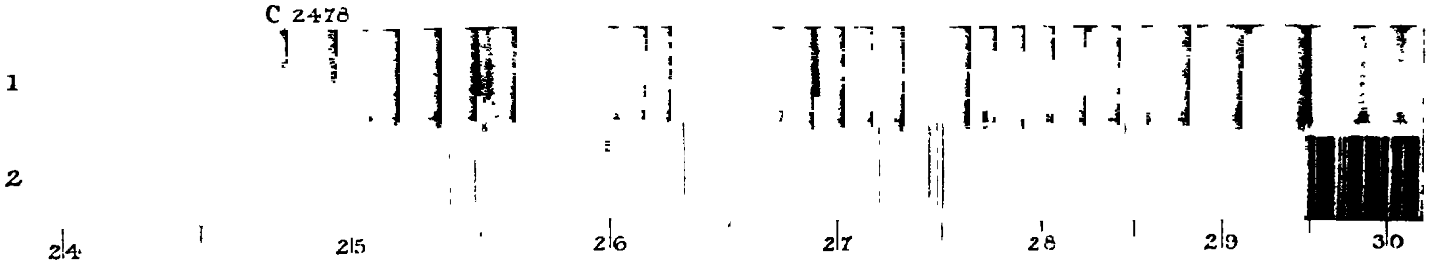
Wave-length.	Intensity.	Group.	Remarks.
2436 ·00	0 ·5	A	
2444 ·56 2445 ·09	2	B	
2453 ·45 2454 ·16	1	A	
2460 ·02 2460 ·07	2	B	
2473 ·21	1	A	
2476 89	2	B	
2493 ·41	4	A	
2508 ·14 2509 ·39	5	?	Indistinct
2511 ·29	6	C	
2522 ·97 2523 ·79	6	D	
2529 90	2	C	
2535 ·54 2536 ·27	2	?	
2538 ·55 2539 ·29	6	D	
2549 ·44	2	C	
2555 ·74 2556 ·10	6	D	
2569 ·61	1	C	
2572 ·64	2	D	
2579 ·12	8	E	
2587 ·26	4	?	
2590 ·22	6	?	
2591 ·93	10	E	
2605 ·59 2606 ·94	8	E	
2621 ·52 2622 ·53	6	E	
2629 ·59 2630 ·70	4	?	
2638 ·85 2639 ·87	4	E	
2059 ·34	2	?	
2661 ·85 2064 ·02	10	F	Very diffuse.
2674 ·66	2	?	
2677 ·44 2679 ·52	8	F	Do.
2692 ·66 2694 ·51	8	F	Do.
2709 ·01 2710 ·41	6	F	
2726 ·62	4	F	
2744 ·49	2	F	
2754 ·78 2756 ·90	6	G	
2769 ·46 2771 ·90	6	G	Indistinct
2785 ·16 2787 ·59	5	G	
2801 ·58 2803 ·58	5	G	
2818 ·37 2819 ·29	4	G	
2837 ·21	4	G	

General Conclusions.

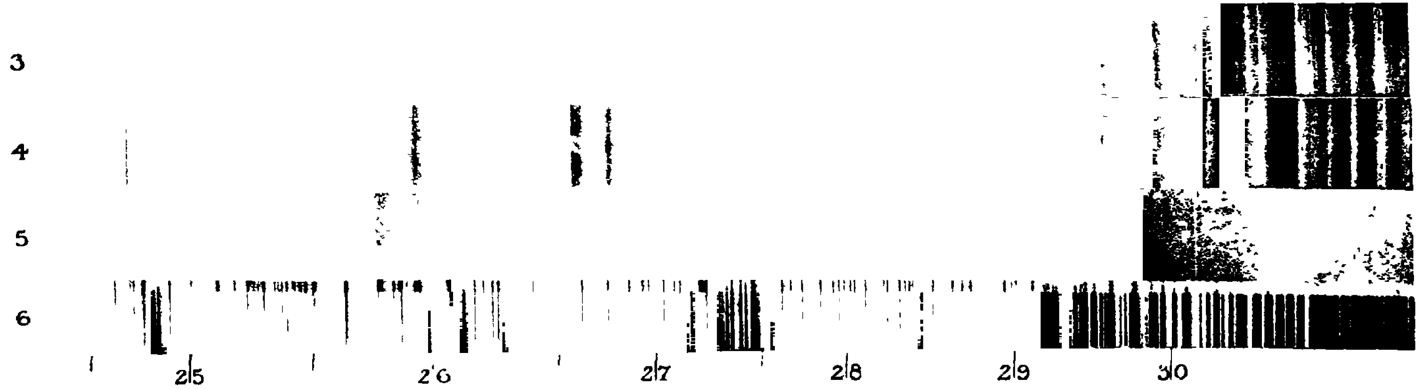
Sir J. Dewar and Dr. H. O. Jones describe an experiment in which the volatile condensable compound produced by the action of the silent electric discharge on the vapour of carbon disulphide is condensed in a U-tube cooled by liquid air. When the tube is removed from the Dewar vessel violent polymerisation occurs, and a flash is produced. The spectrum of this flash is described as containing scattered bands from 2480 to 3620, the sulphur bands between 3840 and 3920, and indications of cyanogen and hydrocarbons. It is probable that, apart from impurities, this spectrum is a reproduction of that produced by the discharge through carbon disulphide vapour, and contains the ordinary sulphur spectrum, together with the bands from 2436 to 2837 described in this paper. The action of the discharge is to break up the vapour into free sulphur and carbon monosulphide. Polymerisation of this monosulphide occurs almost immediately and forms the dark deposit, but during this action the electric discharge, or the influence of great heat, or both as in the electric arc, produces the band system. The different groups vary in their relative development with the conditions of experiment; it is possible that they are due to successive compounds produced during the transition from the disulphide into the monosulphide and its polymers.

The author's best thanks are due to Prof. Fowler, F.R.S., for constant interest during the progress of the experiments, and valuable help during the preparation of the paper.

BAND SPECTRUM DUE TO A SULPHIDE OF CARBON.



1 Electric discharge through carbon disulphide vapour (full exposure)
2 Iron comparison



3 Discharge through sulphur vapour
4 Discharge through carbon disulphide vapour (short exposure).
5. Sulphur in carbon arc
6. Iron comparison.

New Series of Lines in the Spark Spectrum of Magnesium.

By A. Fowler, F.R.S., Assistant Professor of Physics, Imperial College of Science and Technology, South Kensington.

(Received June 12,—Read June 26, 1913.)

Introductory.

A recent investigation suggested that the spectrum of hydrogen was unique in having two Principal series of lines which are related to each other in the same manner as Diffuse and Sharp series.* One of these series begins with a line at λ 4686, and the other with a line at λ 3203, the two series converging to the limit 48764 on the frequency scale. The lines in question have so far only been produced by passing powerful discharges through helium tubes (which also contain hydrogen), but in accordance with the work of Rydberg, they have been attributed to hydrogen on the ground of their series relationship with lines known to be due to hydrogen.

In seeking for further examples of such series, analogy with hydrogen suggested spark spectra as the most promising sources. One of the most remarkable spark lines is the well-known line of magnesium λ 4481, which is ordinarily not visible at all in the arc, but is by far the strongest line in the spark. Further, there is a series of single lines in the arc spectrum of magnesium, first identified as such by Rydberg, which it seemed might possibly be analogous to the Balmer series of hydrogen lines. Magnesium therefore appeared to be a very suitable element for investigation, but existing records of the spectrum were altogether inadequate for the purpose in view. There were, in fact, only two recorded lines which could possibly be connected in series with 4481; namely, the lines given by Exner and Haschek at 3106·5 and 2659·5. Other associated ultra-violet lines, however, have now been photographed, and it results that the spark lines form two series like those of hydrogen, 4481 being analogous to the first Principal line of hydrogen 4686.

Method of Observation.

The magnesium spark lines, as ordinarily obtained, are too diffuse for accurate measurement, and it appears from the present investigation that in the far ultra-violet they are even too diffuse to be recognisable. The lines may be narrowed by the use of self-induction, but they are at the same time weakened, and the more refrangible lines were then too feeble for observation. It is known, however, that the spark lines are also brought out when the arc is passed *in vacuo*; that is, in reality, in a low-pressure atmosphere of hydrogen liberated by the heated metal.* Under these conditions the lines are well developed and sharply defined, and by this method it became possible to photograph five additional lines which were evidently related to the three spark lines already mentioned. The apparatus employed was identical with that described in a previous paper for the observation of the spectrum of magnesium hydride.†

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* 'Monthly Notices R.A.S.,' 1912, vol. 73, p. 62.

In addition to the spark lines, the arc *in vacuo* also exhibits the arc and flame lines, and the bands attributed to magnesium hydride. The spark lines, however, are easily identified by comparison with the arc in air. In the region beyond λ 2540, the five new spark lines are, in fact, the only lines present in most of the photographs.‡

An iron arc comparison was utilised in the determination of wave-lengths, except for the extreme ultra-violet, where, in the absence of tabulated iron lines, the comparison spectrum was that of copper.

The New Series of Spark Lines.

Wave-lengths and other details relating to the new series lines are given in the appended tables. The wave-lengths are on Rowland's scale, and the oscillation frequencies have been corrected to vacuum.

A mere inspection of the photographs suggests that the eight lines form a single series having the usual characteristics, but calculations show that they must be divided into two series by taking alternate lines. As the new series consist of enhanced lines, they may be conveniently designated E_1 and E_2, to distinguish them from the other magnesium series, which already include Principal, Diffuse, and Sharp series of triplets in addition to the Rydberg series of single lines.

The Hicks formulæ for the two series, as calculated from the first three lines in each case, are

$$E_1(m) = 49775{\cdot}81 - \frac{109675}{(m + 0{\cdot}996679 + 0{\cdot}001552/m)^2},$$

$$E_2(m) = 49776{\cdot}30 - \frac{109675}{(m + 0{\cdot}496395 + 0{\cdot}002884/m)^2}.$$

Observed *minus* computed values of the frequencies (O – C) are given in Column 6 of the tables.

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* Fowler and Payn, 'Roy. Soc. Proc.,' 1903, vol. 72, p. 253.

† Fowler, 'Phil. Trans.,' 1909, A, vol. 209, p. 449.

‡ See plate accompanying paper by Fowler and Reynolds, this vol., p. 137

Spark Series E_1.

m.	Wave-length (Fowler).	Limit of error.	Oscillation frequency.	Limit of error.	O−C (frequency).	Remarks.
1	4481·35	0·03	22308·5	0·1	0·0*	Strongest line in spark.
2	2661·00	0·05	37569·0	0·7	0·0*	Exner and Haschek's 2659·5.
3	2329·68	0·05	42911·5	0·9	0·0*	Too diffuse for observation in spark.
4	2202·75	0·05	45383·9	1·0	+0·2	" "

* Used in calculation of constants.

Spark Series E_2.

m.	Wave-length (Fowler).	Limit of error.	Oscillation frequency.	Limit of error.	O−C (frequency).	Remarks.
2	3104·91	0·03	32197·9	0·3	0·0*	Exner and Haschek's 3106·5.
3	2449·68	0·05	40809·7	0·8	0·0*	Very diffuse in spark.
4	2253·94	0·05	44353·3	1·0	0·0*	Too diffuse for observation in spark.
5	2166·35	0·10	46146·4	2·0	−0·3	" "

* Used in calculation of constants.

It will be seen that the calculated limits of the two series are practically identical, and that the values of μ differ by very nearly 0·5, as is also the case with hydrogen. The two spark series of magnesium are accordingly similar to the two Principal series attributed to hydrogen, and run nearly parallel to them, as will be evident from the following comparison of the respective frequencies :—

					Limits.
Mg E_1......	22308·5	37569·0	42911·5	45383·9	(49775·8)
H P I ...	21334·4	36574·7	41907·9	44374·2	(48764·0)
Diff.......	974·1	994·3	1003·6	1009·7	1011·8

					Limits.
Mg E_2......	32197·9	40809·7	44353·3	46146·4	(49776·3)
H P II ...	31208·9	39808·2	43348·4	45137·5	(48763·8)
Diff.......	989·0	1001·5	1004·9	1008·9	1012·5

The similarity not only refers to the distribution of the lines in series, but also, to a considerable extent, to the manner in which the two sets of lines are produced.

Besides the above lines, there are four other magnesium spark lines which do not belong to the series. They are very hazy in the spark itself, but are well defined in the arc *in vacuo.* The wave-lengths of these lines are 4384·86, 4390·80, 4428·20, and 4434·20.

Discussion.

If the new magnesium lines are to be regarded as forming Principal series, the Rydberg-Schuster law of limits would lead us to expect associated Diffuse and Sharp series, with their common limit at 49776 − 22309, *i.e.* at 27467. The Rydberg series of single lines, however, has its limit at 26618, and there is apparently no other series which can be supposed to have any closer relation to the spark lines. In the case of hydrogen there is a similar discrepancy, but of much smaller amount; thus, 48764 − 21334 = 27430, while the limit of the Balmer series is actually at 27418·8. It would thus appear that the Rydberg-Schuster law, in its present form, does not accurately connect the spark series with series produced in the arc. Or it may be that the law fails only when there are two Principal series converging to the same limit.

Attention may be called, however, to another possible relation between the spark and the Rydberg series. If, in the application of the Rydberg-Schuster rule, we use the variable part of the E_2 spark equation given by $m = 1$, in place of the actual limit of the series E_1 and E_2, we get a much closer approximation to the limit of the Rydberg series. Thus, $VE_2(1)$* = 48791, and, if the first line of series E_1 be subtracted from this, it gives 26482, differing by 136 from the limit of the Rydberg series. A still closer approximation is obtained if a simple Rydberg equation be calculated for series E_2, namely, from the first two lines,

$$E_2(m) = 49772{\cdot}4 - \frac{109675}{(m + 0{\cdot}498116)^2}.$$

This gives $VE_2(1) = 48867$, and subtracting 22309 as before, the result is 26558, differing by only 60 from the limit of the Rydberg series.

In view of the approximate character of all series equations, there is thus a strong suspicion that the spark series may be related to the Rydberg series in such a way that the limit of the latter is equal to the difference between the variable part of the equation for the second spark series with $m = 1$ and the frequency of the first line of the first spark series. It should be mentioned, however, that, in the case of hydrogen, the discrepancy is slightly increased if this alteration in the Rydberg-Schuster law be made.

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* In this notation V signifies "variable part" of equation.

Until other examples of spark series have been discovered, it is evident that no definite conclusion can be drawn.

An alternative view would be to suppose that the new series, both in magnesium and hydrogen, are series of a new type, having no necessarily simple relation to other series in the respective spectra. In that case the two series attributed to hydrogen might equally be supposed to belong to helium, the presence of which is necessary for their production in the laboratory; it is difficult to believe, however, that the close agreement of one of the series with the Principal series calculated for hydrogen by Rydberg is merely accidental.

Additional Triplets and other Series Lines in the Spectrum of Magnesium.

By A. Fowler, F.R.S., Assistant Professor of Physics, Imperial College of Science and Technology, South Kensington, and W. H. Reynolds, B.Sc., Research Student.

(Received June 12,—Read June 26, 1913.)

[Plate 7.]

Introductory.

Recent photographs of the spectrum of the magnesium arc *in vacuo*, taken primarily for the investigation of enhanced lines,* have revealed several additional members of the triplet and single line series. For some of the previously known lines it has also been possible to obtain improved wave-lengths on account of their greater sharpness under these conditions. It is believed that the results will form a useful contribution to the general study of series lines, and they have accordingly been brought together in the present communication.

For the representation of the series, the Ritz formula, as modified by Mogendorff† and Hicks,‡ has been employed, namely

$$n = n_\infty - \frac{109675}{(m+\mu+\alpha/m)^2},$$

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* See Fowler, this vol., p. 133.

† 'Roy. Acad. Amsterdam Proc.,' 1906, vol. 9, p. 434.

‡ 'Phil. Trans.,' 1910, A, vol. 210, p. 57.

where n gives the oscillation frequencies of successive lines corresponding to integer values of m; n_∞ is the convergence frequency, or limit, of the series; 109,675 is the general series constant derived from the Balmer series of hydrogen lines; μ and α are constants to be determined for each series. In some cases, it has been necessary to introduce an additional term βm^{-2} in the denominator, as found by Hicks, in order to represent the lines with greater accuracy.

The spectrum of the magnesium arc *in vacuo*, in the visible region, has already been described by Fowler and Payn.* Photographs including the ultra-violet are reproduced in Plate 7. They show the bands attributed to magnesium hydride, together with the lines which are characteristic of the arc, spark, and flame. In the visible spectrum the Rydberg series of single lines is well developed, while in the ultra-violet the triplets and spark lines are striking features. Observations have shown that the spark lines are best developed on the negative pole, while the arc lines are especially conspicuous in the green flame.

In the tables which follow, the wave-lengths are on Rowland's scale throughout, and oscillation frequencies have been reduced to vacuum.

The Diffuse (First Subordinate) Series of Triplets.

Details relating to the Diffuse series of triplets are given in Table I, Kayser and Runge's values being included for comparison so far as they go. The formula calculated for the less refrangible components of the triplets, from the first two and last of the observed members of the series, is

$$\mathrm{D}(m) = 39758{\cdot}72 - \frac{109675}{(m + 0{\cdot}831706 - 0{\cdot}007587/m)^2}.$$

The observed *minus* computed values of the frequencies (O−C) are given in Column 8 and it will be seen that this formula does not represent the series quite within the estimated limits of error, but very nearly so. A more accurate representation of the lines is given by including a term βm^{-2}, namely

$$\mathrm{D}(m) = 39759{\cdot}06 - \frac{109675}{(m + 0{\cdot}825371 + 0{\cdot}023416/m - 0{\cdot}036786/m^2)^2}.$$

As shown in Column 9 (O−C′), the lines are very closely represented by this equation.

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* 'Roy. Soc. Proc.,' 1903, vol. 72, p. 253.

Table I.—The Diffuse Series of Triplets.

m.	K. and R.		F. and R.		Oscillation frequency.	Limit of error	O−C.	O−C′.	Remarks.
	Wave-length.	Limit of error.	Wave-length.	Limit of error.					
1.	2.	3.	4.	5.	6.	7.	8.	9.	10.
1					6708, 6356				Values from the two formulæ.
2	3838·44	0·03			26044·4 (K. R.)	0·2	0·0*	0·0*	Rowland in Sun 3838·44
	32·46	0·03			085·1				„ „ 32·45
	29·51	0·03			105·2				„ „ 29·50
3	3097·06	0·03	3097·03	0·03	32278·8 (K. R.)	0·3	0·0*	0·0*	„ „ 3097·01
	93·14	0·03	93·09	0·03	319·7	0·3			„ „ 93·09
	91·18	0·03	91·19	0·03	340·2	0·3			„ „ 91·18
4			2851·76	0·03	35056·0	0·4	−1·1	+0·3	Separated from strong line 2852·22 in 2nd order grating photograph
	2848·53	0·15	48·54	0·03	095·0	0·4			
	46·91	0·15	46·88	0·03	114·9	0·4			
5	2736·84	0·15	2736·63	0·03	36530·7	0·4	−1·5	0·0	
	33·80	0·15	33·64	0·03	570·7	0·4			
	32·35	0·15	32·16	0·03	590·5	0·4			
6	2672·90	0·20	2672·53	0·03	37406·8	0·4	−1·2	−0·0	
	69·84	0·20	69·66	0·03	447·0	0·4			
	68·26	0·20	68·24	0·03	467·0	0·6			
7	2633·13	1·00	2632·98	0·03	37968·8	0·4	−1·3	−0·4	
	30·52	1·00	30·14	0·03	38009·8	0·4			
			28·73	0·03	030·1	0·4			
8	(2605·4)		2606·73	0·05	38351·0	0·7	−1·3	−0·7	
			03·98	0·05	391·5	0·7			
			02·59	0·05	412·1	0·7			
9			2588·37	0·05	38623·0	0·7	−0·9	−0·5	
			85·63	0·05	664·0	0·7			
			84·32	0·05	683·6	0·7			
10			2575·02	0·05	38823·4	0·7	−0·4	−0·1	
			72·03	0·05	863·8	0·7			
			70·96	0·10	884·7	1·4			
11			2565·00	0·05	38974·9	0·7	−0·3	−0·1	
			62·30	0·05	39016·0	0·7			
			60·96	0·10	036·5	1·4			
12			2557·29	0·05	39092·5	0·8	−0·1	0·0	Third member not observed.
			54·70	0·10	132·6	1·6			
13			2551·22	0·05	39185·4	0·8	0·0*	0·0*	„ „ „
			48·56	0·10	226·2	1·6			

* These lines were used in the calculation of constants.

The Sharp (Second Subordinate) Series of Triplets.

Details of the Sharp series of triplets are given in Table II. The formula calculated for the less refrangible components from the first three and the last line is

$$S(m) = 39759{\cdot}18 - \frac{109675}{(m + 1{\cdot}375125 - 0{\cdot}058307/m - 0{\cdot}002355/m^2)^2}.$$

Following Hicks, a term βm^{-2} has been introduced for the better representation of this series, and μ has been taken greater than unity.

It will be seen that the eight lines are represented almost perfectly by the equation given above, and the limit of the series only differs by

Table II.—The Sharp Series of Triplets.

m	K. and R.		F. and R.		Oscillation frequency	Limit of error.	O−C (frequency).	Remarks.
	Wave-length.	Limit of error.	Wave-length.	Limit of error.				
1	5183·84	0·03			19285·0	0·1	0·0*	Rowland in Sun 5183·79
	72·87	0·03			325·9			„ „ 72·86
	67·55	0·03			345·8			„ „ 67·50
2	3336·83	0·03			29959·4	0·3	0·0*	„ „ 3336·82
	32·28	0·03			30000·3			„ „ 32·33
	30·08	0·03			020·1			„ „ 30·04
3	2942·21	0·3			33977·6	0·3	0·0*	
	38·67	0·3			34018·5			
	36·99	0·3			038·0			A strong line near at 2936·61
4			[2781·43]		[35942·3]		0·0†	
			[2778·27]		[983·2]			
			[2776·73]		[36003·2]			
5	2698·44	0·15	2698·23	0·03	37050·5	0·4	−0·15	
	95·53	0·15	95·28	0·03	091·1			
	93·97	0·15	93·85	0·03	110·8			
6	2649·30	0·50	2649·12	0·03	37737·4	0·4	−0·1	
	46·61	0·50	46·27	0·05	778·0	0·7		
	45·22	0·50	44·88	0·10	797·9	1·5		
7			2617·57	0·03	38192·4	0·4	0·0	Third member not observed.
			14·74	0·05	233·6	0·7		
8			2596·01	0·03	38509·4	0·4	0·0*	„ „ „
			93·28	0·05	550·0	0·7		

* Used for the calculation of constants.

† The wave-lengths in Column 4 for this triplet were calculated from the formula. The triplet falls in a group of five relatively strong lines, and its components appear to be masked by lines for which the wave-lengths are 2781·62, 2778·39, 2776·80. The other two neighbouring lines are 2783·08, 2779·94.

0·12 from the limit calculated for the Diffuse series when the term βm^{-2} is introduced.

As regards the agreement of the observed and calculated values, however, an almost equally good result is obtained by taking μ less than unity, so that m is 2 for 5183·84. Using the same lines as before the equation then becomes

$$S(m) = 39760{\cdot}48 - \frac{109675}{(m + 0{\cdot}361817 + 0{\cdot}039793/m - 0{\cdot}269293/m^2)^2}.$$

The limit is scarcely changed, and the differences O−C are respectively 0·0, 0·0, 0·0, (?), +0·6, +0·5, +0·2, 0·0. Applying Rydberg's law this equation would lead us to expect an ultra-violet series, the limit of which (obtained by putting $m = 1$) would be at 85540, and the first line of the first triplet at 45780 ($\lambda = 2184{\cdot}36$). The observations include the region which would be occupied by this triplet, but the lines have not been observed.

Hence, the first equation is probably correct, as Rydberg's law then indicates a principal series of triplets in the infra-red with its limit at 39759−19285 = 20474. This series has apparently been observed by Paschen,[*] and the limit calculated from the actual lines observed is given by him as 20466·7.

From the data given the mean interval between the first and second members of the triplets in the Diffuse and Sharp series is 40·6, and that between the second and third 20·1. The formulæ connecting the second and third components may accordingly be deduced by subtracting 40·6 and 60·7 from the first terms of the equations representing the first members of the triplets given above.

The Rydberg Series.

As produced in the arc in air, the lines of the Rydberg series of single lines are very diffuse, especially on their less refrangible sides, and except for the first few lines the wave-lengths have not previously been determined with any great degree of accuracy. The arc *in vacuo* gives them quite sharply, and advantage has been taken of this to get better values for the wave-lengths. In Table III the first line is from Paschen; the next three are from Rowland's solar tables; the next four were determined from a photograph of the arc *in vacuo* taken with a 10-foot concave grating, and the last three from photographs with a prismatic spectroscope.

This series has long been recognised as one which cannot be accurately represented by a formula, and the revised wave-lengths provide a further test. The Hicks equation calculated from the first three and last lines of the observed spectrum is

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[*] 'Ann. der Phys.,' 1909, (4), vol. 29, p. 652.

$$\mathrm{R}_1(m) = 26618{\cdot}20 - \frac{109675}{(m + 0{\cdot}314582 + 0{\cdot}899929/m - 0{\cdot}269730/m^2)^2}.$$

The differences, "observed − computed" frequencies, are shown in Column 8.

Table III.—The Rydberg Series of Single Lines.

m.	Previous measures.		F. and R.		Oscillation frequency.	Limit of error.	O − C.	Remarks.
	Wave-length.	Limit of error.	Wave-length.	Limit of error.				
2	8807·3 P.				11351·1 P.		−186·7	P. = Paschen.
3	5528·64 R.				18082·7 R.		0·0*	R. = Rowland.
4	4703·18 "				21256·4 "		0·0*	K. R. = Kayser and
5	4352·08 "				22971·1 "		0·0*	Runge.
6	4167·81 K. R.	0·10	4167·55	0·02	23988·2 F. R	0·1	+0·5	F. R. = Fowler and
7	4058·45 "	1·00	4057·78	0·02	24637·1 "	0·1	+1·5	Reynolds.
8	3987·08 "	1·00	3986·94	0·02	25074·8 "	0·1	+2·5	
9			3938·58	0·03	25382·7 "	0·2	+2·8	
10			3904·17	0·05	25606·3 "	0·3	+1·7	
11			3878·73	0·05	25774·3 "	0·3	+0·9	
12			3859·30	0·10	25903·5 "	0·7	0·0*	

* Used in the calculation of constants.

It will be observed that even a four-constant formula does not represent all the observed lines within the limits of error, and that extrapolation to the infra-red member of the series ($m = 2$) is very defective. Further, the negative value obtained by putting $m = 1$ is 2379·7, and this is far from being in agreement with the infra-red line of frequency 5843·6 ($\lambda = 17108{\cdot}1$), which Paschen regards as connected with the Rydberg series. If the infra-red line λ 8807 and the three following lines are used for calculation, the formula becomes

$$\mathrm{R}_1(m) = 26635{\cdot}40 - \frac{109675}{(m + 0{\cdot}253055 + 1{\cdot}247337/m - 0{\cdot}790662/m^2)^2},$$

giving O − C, 0·0*, 0·0*, 0·0*, 0·0*, −1·9, −3·6, −5·0, −6·4, −9·2, −11·2, −13·0. The negative value obtained by putting $m = 1$ is now 10883·7, in place of the closer approximation to 5843·6, which might have been expected from the lines employed for calculation.

It is evident that the formulæ given above do not well represent the Rydberg series as a whole. The limit of the series, however, is not likely to be far from the value given by the first formula, namely, 26618·2.

[*Note.*—An interesting result, which follows from the revision of the wave-lengths of the lines of the Rydberg series, is the identification of four additional strong solar lines with lines of magnesium. The details are as follows, including the three lines previously identified by Rowland:—

Table IV.—Rydberg Series in Solar Spectrum.

K. and R.		F. and R.		Rowland.			
Wave-length.	Limit of error	Wave-length.	Limit of error.	Wave-length in arc.	Wave-length in Sun.	Intensity in Sun.	Remarks.
5528·75	0·10			5528·67	5528·64	8	Previously identified in Sun as Mg
4703·33	0·05			4703·25	4703·18	10	
4352·18	0·05				4352·08	5	
		4167·55	0·02		4167·44	8	No origin assigned to solar line by Rowland.
		4057·78	0·02		4057·67	7	" " "
		3986·94	0·02		3986·90	6	" " "
		3938·58	0·03		3938·55	4	" " "

It will be seen that the wave-lengths in the sun are consistently lower than the wave-lengths in the arc, but this may perhaps be accounted for by the unsymmetrical character of the arc lines, which are shaded towards the red, and would produce a displacement to the side of longer wave-lengths in the arc measurements. There can be no doubt that the four important solar lines in question should be assigned to magnesium. The remaining lines of the Rydberg series cannot be traced with certainty in the solar spectrum, on account of their superposition on iron lines.]

Other Probable Series of Single Lines.

There are two other magnesium arc lines which appear to be related to the Rydberg series, though no connection has hitherto been recognised. Their wave-lengths, as given by Kayser and Runge, are 5711·56 and 4730·42. Assuming that the two lines are successive members of a series, a simple Rydberg formula gives the limit of the series as 26632·1, which is very nearly that of the Rydberg series. If the limit then be assumed to be identical with that of the Rydberg series (26618·2), a Hicks formula indicates a third line about λ 4354. This line has not previously been recorded, but it is readily seen in photographs of the ordinary magnesium arc taken with adequate exposure and dispersion; its wave-length is 4354·53 ± ·05. The three lines are all of the same character as those of the Rydberg series, but much weaker, and their intensities diminish in passing to the violet in the manner characteristic of series lines. The first line is identified by Rowland with the solar line 5711·31; the second is doubtless identical with the solar line 4730·21, though it is not assigned to magnesium by Rowland; and the third is probably identical with the solar line 4354·43. Adopting the solar wave-lengths as the best approximation to the true wave-lengths of the lines, the Hicks formula is

$$R_2(m) = 26620{\cdot}65 - \frac{109675}{(m + 0{\cdot}479157 - 0{\cdot}032160/m)^2}.$$

Details as to the lines are given in Table V.

Table V.—The Second Series of Single Lines.

m.	K. and R.		F. and R.		Rowland.		Oscillation frequency (Rowland).	Remarks.
	Wave-length.	Limit of error.	Wave-length.	Limit of error.	Wave-length in Sun.	Intensity in Sun.		
2							8542·6	Calculated from formula.
3	5711·56	0·15			5711·31	6	17504·3	
4	4730·42	0·25	4780·34	0·05	4730·21	2	21134·9	
5			4354·53	0·05	4354·43	0 Nd?	22958·8	

The equation for this series suggests that it is of the Sharp or second subordinate type, while the Rydberg series is the associated Diffuse or first subordinate series. If this be so, the variable part of the equation when $m = 1$ might be expected to approximate to the limit of the related Principal series, if such a series exists. The variable part is actually 52380, and the first line of the Principal series would be expected at 52380 − 26620 = 25760, *i.e.* at λ 3882. There is, however, no appropriate line near this position. In another paper* it is suggested that the Principal series may be the newly recognised spark series beginning at λ 4481 (frequency 22308·5), but this is far from agreeing with the foregoing calculation. It is not impossible that the first member of the Principal series sought for may be the strong arc line λ 2852 (frequency 35056), but the discordance would then be even greater than for the spark series. A formula capable of more general application in the representation of series is greatly to be desired.

For completeness, it should be recalled that there is a feebly developed series of lines which is also associated with the Rydberg series.† The wave-

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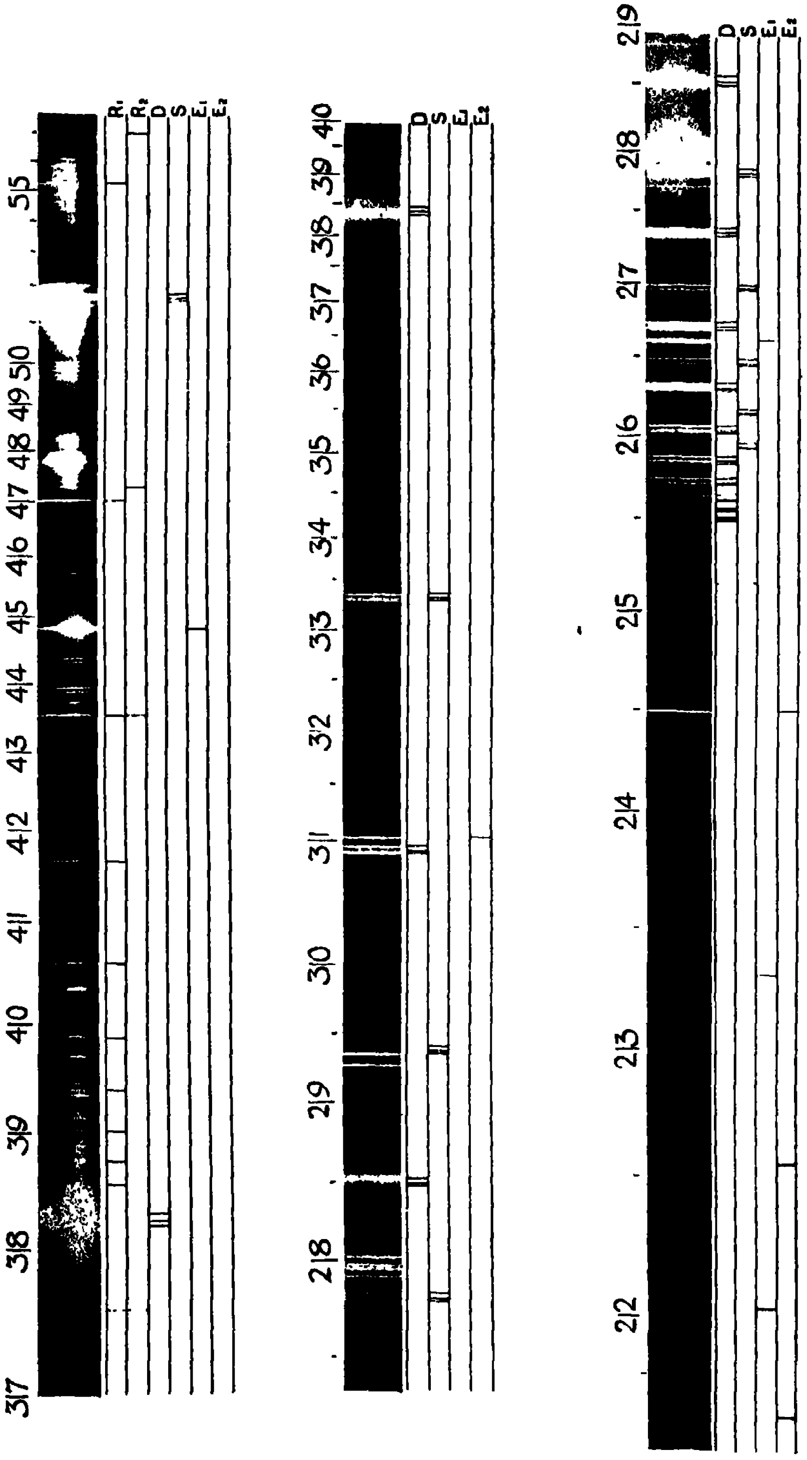
* Fowler, *loc. cit.*

† Fowler, 'Roy. Soc. Proc.,' 1903, vol. 71, p. 420.

Fowler & Reynolds. *Roy. Soc. Proc. A, vol. 89, Pl. 7.*



Spectrum of Magnesium Arc in vacuo.

lengths of these lines are about 4511·4, 4251·0, 4106·8, 4018·3. A Hicks equation, calculated from the first three lines, gives the limit of the series as 26633·2, while if the term βm^{-3} be introduced by using all four lines the calculated limit is 26613·0. These are as near to the limit of the Rydberg series as can be expected from the approximate wave-lengths which can alone be obtained. The series may be regarded as a third subordinate one.

Summary.

1. Eight additional triplets have been measured in the spectrum of the magnesium arc *in vacuo*, six of which belong to the Diffuse and two to the Sharp series. For some of the previously known lines improved wave-lengths have also been obtained.

2. Four additional members of the Rydberg series of single lines have also been photographed. Even a four-constant formula does not accurately represent this series.

3. Four strong solar lines of previously unknown origin have been identified with lines of the Rydberg series, namely, 4167·44, 4057·67, 3986·90 3938·55.

4. A previously unrecorded line at 4354·53 may be united in a series with the known lines 5711·31 and 4730·21 having the same limit as the Rydberg series. This series is probably of the Sharp or second subordinate type.

DESCRIPTION OF PLATE.

The photographs show the spectrum of the magnesium arc *in vacuo* between wave-lengths 5750 and 2160, and indicate the various series in which the lines have been classified. The letters at the side have the following significance:—

R_1, Rydberg series of single lines.
R_2, Probable second subordinate to Rydberg series.
D, Diffuse (1st sub.) series of triplets.
S, Sharp (2nd sub.) series of triplets.
$\left.\begin{matrix}E_2\\E_1\end{matrix}\right\}$ Series of spark lines.

In addition to lines of magnesium, the photographs show the magnesium hydride bands in the neighbourhood of 560, 521, and 480, and a background of faint lines due to the same substance. There are also a few lines due to impurities of calcium, iron, and manganese, the most prominent being those of calcium at 3934, 3968, and 4227.

A New Band Spectrum Associated with Helium.[*]

By W. E. Curtis, B.Sc., A.R.C.S., D.I.C., Demonstrator of Astrophysics at the Imperial College of Science, South Kensington.

(Communicated by A. Fowler, F.R.S. Received June 12,—Read June 26, 1913.)

[Plate 8.]

Introductory.

In the course of Prof. Fowler's recent observations of the principal series of hydrogen lines in the spectra of helium tubes[†] traces were frequently seen of a band spectrum the origin of which was unknown, and of which no previous record could be found.[‡]

The most prominent features visually were bands having their heads at about λλ 6400, 5732, 4649, and 4626. The band at 5732 was degraded towards the violet end of the spectrum, the opposite being the case with the other three. Although in the first instance the new bands were always comparatively feeble, they were such a frequent and persistent feature of the spectra of the various tubes that it was thought desirable to investigate their origin, and to determine their positions. It was soon found possible, by choosing suitable conditions of pressure and discharge, to obtain the new spectrum quite brightly, when a number of other bands were observed, some visually and others by photography. These bands were evidently associated with those first noticed.

Conditions of Observation.

The discharge tubes employed were mostly of the ordinary Plücker form, and were sealed on to an apparatus consisting of a tube containing cleveite, potash and phosphorus pentoxide tubes, and a charcoal bulb. After the whole apparatus had been exhausted by means of a Gaede pump the cleveite was heated, and the gases given off were passed over the potash and phosphorus pentoxide into the vacuum tube. The charcoal was then cooled with liquid air, and absorption allowed to proceed until no further changes were observed in the spectrum. The discharge was kept running for some hours in order to clear off as much gas as possible from the electrodes. It may be mentioned that as far as carbon impurities were concerned this treatment proved very effective. Several tubes prepared in this way and then sealed off show no trace of carbon bands after a great deal of use. Hydrogen, however, could not be eliminated in this way. The new spectrum was not seen until the carbon (Ångström) bands had practically disappeared, leaving the helium lines the predominant feature of the spectrum, with hydrogen present in small quantity, and frequently some mercury. The pressure of the helium in the tube depended upon the amount of heating to which the cleveite had been subjected. In most cases it was reheated several times, and absorption allowed to proceed to the limit in each case.

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[*] Shortly after this paper was communicated to the Society a reprint of a paper describing the same spectrum was received from Dr. E. Goldstein. It bears the title "Über ein noch nicht beschriebenes, anscheinend dem Helium angehörendes Spektrum" ('Deut. Phys. Ges.,' vol. 15, p. 10). Dr. Goldstein's results appear to have been obtained under conditions very similar to those described in the present paper, and the two accounts of the spectrum are in close agreement.

[†] A. Fowler, 'Monthly Notices R.A.S.,' 1912, vol. 73, p. 62.

[‡] While the present investigation was in progress it was found that a band spectrum had been observed by W. Heuse in the positive column of the discharge in a helium tube of wide bore ('Deut. Phys. Ges.,' 1900, vol. 2, p. 16). The spectrum was there attributed to helium, but no description or measurements were given.

As a result of the examination of a number of sealed tubes containing various gases (helium chiefly in nine cases) it appears that the following are the principal facts bearing on the development of the new bands:—

(1) The only substances common to all the tubes from which the new spectrum was obtained were helium and hydrogen, the former being the chief constituent in every case.

(2) A moderately high pressure is desirable; the best results were obtained when the pressure was just too high to permit of the formation of the Crookes dark space round the cathode.

(3) With an uncondensed discharge (*i.e.*, with no capacity in the secondary circuit) the new bands were faintly visible both in the capillary and the bulbs. They could be obtained very much more brightly, however, on introducing a little capacity and a short spark-gap (1 or 2 mm.), but then appeared only in the bulbs. On increasing the current through the tube beyond a certain limit, either by lengthening the spark-gap or by increasing the capacity, the new spectrum began to decrease in relative intensity.

(4) The evident association of the new spectrum with that of helium suggested that it might possibly occur in celestial spectra showing the lines of the latter element. An examination of a number of such spectra has accordingly been made, but without result.

Description of the New Spectrum.

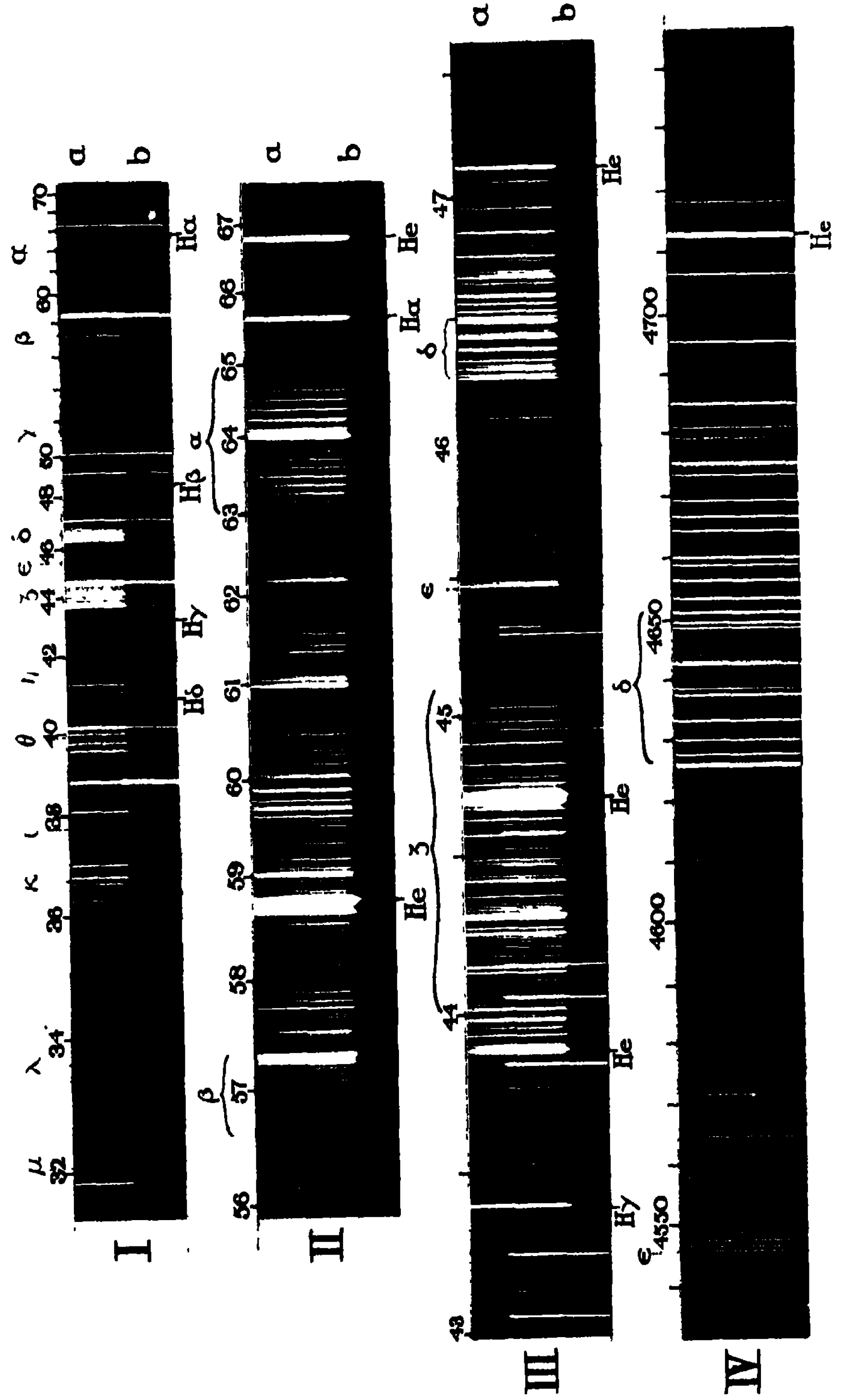
The wave-lengths given are only approximate, as the bands are in many cases of such a nature that the precise positions of the heads could only be determined after a complete analysis of the spectrum. The bands are degraded towards the less refrangible side in every case save one, this exception being that marked β, and having its head about 5732.

Wave-length (I.A.).	Reference letter in Plate.	Remarks.
6399	α	Very strong head.
6310		Companion head ill-defined, but probably about here.
6250 to 5750		Many obvious band-lines in this region, but no easily recognisable heads.
5732	β	Very strong single head; band degraded towards violet.
5133·7 5112	γ	Although weak in photographs, these heads are fairly conspicuous visually.
5056·1		Faint single head.
4648·55 4625·63	δ	Very strong heads; bands well developed.
4546·4	ϵ	Strong single head.
4500 to 4400	ζ	Many strong lines, but no obvious heads.
4157·8	η	Fairly strong single head.
4050 to 3900	θ	Many strong lines; positions of heads uncertain.
3777	ι	Fairly strong single head.
3677 3665	κ	Strong double head.
3356·5 3348·5	λ	Fairly strong double head.
3206 3201	μ	Rather weak double head.
3123 3118		Very weak double head; too faint to show in reproduction.

Probable Origin of the Spectrum.

In the present state of the experimental evidence it seems reasonable to attribute the new spectrum to helium, but further work will be necessary before the question of its origin can be regarded as definitely settled. The matter is complicated by the presence of hydrogen in all the tubes examined; if this could be completely removed, and the new spectrum were found to persist, there would be no reason to suppose that any substance other than helium is concerned in its production. Up to the present, however, attempts to get rid of the hydrogen have not been successful, so that it is necessary to admit the possibility of hydrogen being connected with the origin of the bands.

It may be remarked here that the presence of hydrogen may easily be overlooked unless a careful examination is made. For example, a tube may show no trace of the hydrogen lines either in capillary or bulb when the uncondensed discharge is employed, and show them fairly strongly in the bulbs on introducing the condenser, yet still give no trace of them in



A New Band Spectrum associated with Helium the capillary. An incidental illustration of such a case will be found in Plate 8, I.

I am greatly indebted to Prof. Fowler for the constant interest he has taken in this work.

DESCRIPTION OF PLATE.

I (*a*). New spectrum, showing also the helium and hydrogen lines.
(*b*). Helium comparison, obtained from capillary of same tube with uncondensed discharge. Note complete absence of hydrogen lines in this case.
II (*a*) and III (*a*). Portions of new spectrum (with lines of helium and hydrogen) taken on a Littrow prismatic spectrograph.
II (*b*) and III (*b*). Iron arc comparisons.
IV. Portion of new spectrum taken in first order of 10-foot Rowland concave grating, showing structure of bands δ and ε.

Studies on the Processes Operative in Solutions (XXX) *and on Enzyme Action* (XX).—*The Nature of Enzymes and of their Action as Hydrolytic Agents.*

By E. Frankland Armstrong and H. E. Armstrong, F.R.S.

(Received June 13,—Read June 26, 1913.)

[This paper is printed in Series B, vol. 86, No. 591.]

On Trigonometrical Series whose Cesàro Partial Summations Oscillate Finitely.

By W. H. YOUNG, Sc.D., F.R.S., Professor of Mathematics in the University of Liverpool.

(Received May 21,—Read June 19, 1913.)

§ 1. Riemann's remarkable theorem, which, in the extended form given to it by Lebesgue, by virtue of the use of the concept of generalised integration, asserts that a trigonometrical series is a Fourier series if it converges everywhere, except at a reducible set of points, to a function which is summable and has a value, or values, everywhere finite, has been discussed, and still further extended, by a relatively large number of writers.* The object of the present communication is to state and prove certain results which include all those at present known. They are as follows:—

I. *If the upper and lower functions of the succession of the Cesàro partial summations, index not greater than unity, of a trigonometrical series*

$$\sum_{r=1}^{\infty}(a_r\cos rx+b_r\sin rx)\equiv\sum_{r=1}^{\infty}A_r,$$

which is such that $a_n\to 0$ *and* $b_n\to 0$ *as* $n\to\infty$, *are summable, and everywhere finite except possibly at a set of points which contains no perfect sub-set, then the series is a Fourier series.*

II. *If the upper and lower functions of the succession of the Cesàro partial summations, index* k $(0\leq k<1)$, *of a trigonometrical series* $\sum_{r=1}^{\infty}A_r$, *are summable and everywhere finite, then the series is a Fourier series.*

§ 2. In the proof of these results all turns on the use of upper and lower derivates of a generalised character. If $f(x)$ denote the function, it is open to us to consider, not merely the limits of

$$[f(x+h)-f(x-h)]/2h,$$

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* It will be sufficient for the purpose of the present communication to refer to the following:—W. H. Young, "On the Conditions that a Fourier Series should have the Fourier Form," 'Lond. Math. Soc. Proc.,' 1910, Series 2, vol. 9, pp. 421–433; Marcel Riesz, "Ueber summierbare trigonometrische Reihen," 'Math. Ann.,' 1911, vol. 71, pp. 54–75; De la Vallée Poussin, "Sur l'Unicité du Développement Trigonométrique," 'Bull. de l'Acad. Royale de Belgique,' 1912, pp. 702–718, and *ibid.*, 1913, pp. 9–14. We shall also have occasion to refer to L. Fejér, "Untersuchungen über Fourier'sche Reihen," 'Math. Ann.,' 1903, vol. 58, pp. 51–69.

for example. We may, as is well known, consider with advantage the limits of the expression obtained from this formally by integrating numerator and denominator with respect to h separately between the limits 0 and h. The expression so obtained, though not conceived of in this manner, has indeed formed the subject of considerable discussion. No one appears, however, to have seen the advantage that could be obtained from the consideration of the expressions obtained when the process in question is repeated. L. Fejér, in his very valuable paper,[*] employs in fact an entirely different expression which has not the simple properties of those here referred to. By a known theorem in the theory of indeterminate forms such expressions as those made use of in the present communication have at each stage limits lying between the limits of each of the expressions obtained at a lower stage.

This fact enables us to see that the higher expressions share the striking properties shown by de la Vallée Poussin to be possessed by

$$\{F(x+h)+F(x-h)-2F(x)\}/h^2.[†]$$

A modification of Fejér's reasoning is then all that is required to obtain the main theorem from which the first of the results given in § 1 immediately follows.

To obtain the second of the results we have then merely to make use of certain simple facts in the theory of Cesàro summation, due essentially to Knopp and Marcel Riesz, though not as far as I am aware explicitly stated by them.

§ 3. As regards the importance of the results here exposed, this does not consist merely in the fact that they include previous results as special cases. This will be evident if we reflect on the part played by Cesàro summation in the theory of Fourier series. We know practically nothing about the mode of convergence, or oscillation, of a Fourier series when summed in the ordinary manner, except in one or two isolated instances. On the other hand, all such series converge almost everywhere when summed in any Cesàro manner. Thus, the upper and lower functions of such Cesàro partial summations have the same degree of summability as the function corresponding to the Fourier series, differing, in fact, from it only at a set of content zero. That the most general results hitherto obtained, those due to de la Vallée Poussin, remarkable as they are, are not final, is then at once evident. It should not be necessary to have information with regard to the ordinary upper and lower functions, in order to say whether a trigonometrical series is a Fourier series; it should be sufficient to have the corresponding information with regard to the Cesàro partial summations. It is precisely this step which the results of the present communication enable us to take. Moreover, in this way the investigations which took their rise in Riemann's paper take a more or less final form which brings them into formal analogy in some sort with the necessary and sufficient conditions I have shown to hold that a trigonometrical series should be the Fourier series of a function of a certain type. These necessary and sufficient conditions are, in fact, expressed in the language of Cesàro summations.

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[*] *Loc. cit., supra.* Marcel Riesz's interesting investigations (*loc. cit.*) are closely connected with Fejér's.

[†] *Loc. cit., supra.*

The interest is further enhanced if we appeal to the analogy between the properties of Fourier series when summed in the Cesàro manner with the properties of derivates. The analogy is a striking one. Thus we have the pair of theorems:—

If a function is an integral, its upper and lower derivates agree except at a set of content zero. (Lebesgue.)

If a trigonometrical series converges to an integral, the upper and lower functions of its derived series, when summed in any Cesàro manner, agree except at a set of content zero.

Lebesgue's Theorem remains true when for an integral we write a function of bounded variation, and I have recently shown that the same is true of the analogous theorem.

We are thus naturally led to inquire whether the counterpart of Lebesgue's Theorem, also proved by him, has its correspondent in the theory of Fourier series. The present paper enables us to answer this question in the affirmative, and in this way to complete the analogy. We have, in fact, the following pair of theorems:—

If the derivates of a function are summable and finite everywhere, the function is an integral. (Lebesgue.)

If the upper and lower functions of the derived series of a trigonometrical series, when summed in some Cesàro manner of positive index less than unity, are summable and finite everywhere, the trigonometrical series converges to an integral.

Moreover, corresponding to the known extension of Lebesgue's Theorem to which I have called attention, in which exceptional points are permitted, we have a corresponding extension of its analogue in the theory of Fourier series.

§ 4. We shall now obtain the theorem which corresponds to that proved by Fejér.* I give it in a form which we can at once apply.

Theorem.—*If*

$$\mathrm{F}(x) = -\sum_{r=1}^{\infty}(a_r \cos rx + b_r \sin rx)/r^2 = -\sum_{r=n}^{\infty} \mathrm{A}_r/r^2,$$

and

$$\mathrm{K}(x) = \sum_{r=1}^{\infty} \mathrm{A}_r/r^4,$$

the former series, and therefore the second, necessarily converging by virtue of a subsequent condition, and if by S (x) *we denote the upper function of the succession of the moduli of the partial summations of* $\sum_{r=1} \mathrm{A}_r$ *when summed in the Cesàro manner, index unity, then the limits of*

$$\mathrm{G}(h) = [\mathrm{K}(x+h)+\mathrm{K}(x-h)-2\mathrm{K}(x)-h^2\mathrm{F}(x)]/\tfrac{1}{12}h^4,$$

as $h \to 0$, *are numerically less than* $k\mathrm{S}(x)$, *where* k *is a constant independent of* x, *it being here assumed that* S (x) *is finite at the point considered.*

We have

$$\mathrm{K}(x+h)+\mathrm{K}(x-h)-2\mathrm{K}(x) = -\sum_{r=1} 2(1-\cos rh)\,\mathrm{A}_r/r^4,$$

whence

$$\mathrm{G}(h) = \sum_{r=1} \mathrm{A}_r[r^2h^2-2(1-\cos rh)]/\tfrac{1}{12}r^4h^4 = \sum_{r=1} \mathrm{A}_r\phi(rh), \text{ say,}$$

so that

$$\operatorname*{Lt}_{t\to 0} \phi(t) = \operatorname*{Lt}_{t\to 0} 2(t-\sin t)/\tfrac{1}{3}t^3 = 1.$$

Now write

$$s_n = \sum_{r=1}^{n} \mathrm{A}_r \qquad \mathrm{S}_n = \sum_{r=1}^{n} s_r/n.$$

Hence

$$\mathrm{G}(h) = \operatorname*{Lt}_{m\to\infty} \sum_{r=1}^{m} \mathrm{A}_r\phi(rh) = \operatorname*{Lt}_{m\to\infty}[s_1\phi(h)+(s_2-s_1)\phi(2h)+\ldots+(s_m-s_{m-1})\phi(mh)]$$

$$= \operatorname*{Lt}_{m\to\infty}[s_1\{\phi(h)-\phi(2h)\}+\ldots+s_{m-1}\{\phi(\overline{m-1}\,h)-\phi(mh)\}+s_m\phi(mh)]$$

$$= \sum_{r=1}^{\infty} s_r\{\phi(rh)-\phi(\overline{r+1}\,h)\},$$

since, by § 5, *infra*, s_m/m is bounded, and $m\phi(mh)$ for fixed h vanishes as $m \to \infty$. Thus

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* *Loc. cit.*, pp. 62–65. Fejér's theorem states that "if Σc_n converges (C1) and $s_n = \sum_{n=0}^{n} c_n$, $\mathrm{S}_n = \dfrac{s_0+s_1+\ldots+s_n}{n+1}$, and if $|\phi(t)| < \mathrm{M}/t^{2+\rho}$, $|\phi''(t)| < \mathrm{M}/t^{2+\rho}$ when $0<t<1$, then $\mathrm{F}(t) = \sum_{n=0}^{\infty} u_n\phi(nt)$ converges for every positive value of t, and if $\phi(0) = 1$, the limit of its sum when $t_1 \to 0$ is the Cesàro sum of the series Σc_n."

$$G(h)=\underset{m\to\infty}{\mathrm{Lt}}[S_1\{\phi(h)-\phi(2h)\}+\ldots$$
$$+\{mS_m-(m-1)S_{m-1}\}\{\phi(mh)-\phi(\overline{m+1}h)\}]$$
$$=\underset{m\to\infty}{\mathrm{Lt}}[S_1\{\phi(h)-2\phi(2h)+\phi(3h)\}+2S_2\{\phi(2h)-2\phi(3h)+\phi(4h)\}+\ldots$$
$$+(m-1)S_{m-1}\{\phi(\overline{m-1}h)-2\phi(mh)+\phi(\overline{m+1}h)\}$$
$$+mS_m\{\phi(mh)-\phi(\overline{m+1}h)\}].$$

Now S_m has finite upper and lower bounds at the point x considered, while $m\phi(mh)$ and $m\phi(\overline{m+1}\,h)$ have each the unique limit zero as $m\to\infty$, therefore the final term on the right of the last expression vanishes as $m\to\infty$. Hence

$$G(h)=\sum_{r=1} rS_r\{\phi(rh)-2\phi(\overline{r+1}h)+\phi(\overline{r+2}h)\}.$$

Now we can find a point X_r internal to the interval $\{rh, (r+2)h\}$ so that

$$|\phi(rh)-2\phi(\overline{r+1}h)+\phi(\overline{r+2}h)|\leq 2h^2|\phi''(X_r)|.$$

Therefore

$$|G(h)|\leq\sum_{r=1} r|S_r|2h^2|\phi''(X_r)|, \qquad [rh<X_r<(r+2)h],$$
$$\leq\sum_{r=1}^{M} r|S_r|2h^2|\phi''(X_r)|+\sum_{r=M+1}^{N} r|S_r|2h^2|\phi''(X_r)|+\sum_{r=N+1}^{\infty} r|S_r|2h^2|\phi''(X_r)|,$$

where M is a number independent of h, but depending on e, such that, for values of $n>M$, S_n lies between $u(x)+e$ and $l(x)-e$, whence, denoting by S the greater of $|u(x)|$ and $|l(x)|$,

$$|S_r|<S+e, \qquad (M<r),$$

and N is such that $$(N-1)h\leq 1<Nh.$$

We can confine our attention to values of h so small that $Mh<1$, and therefore $M<N$.

Now $$\phi(t)/12=t^{-2}-2(1-\cos t)t^{-4}.$$
Therefore

$$\phi''(t)/12=6t^{-4}-2\cos t\,.\,t^{-4}+16\sin t\,.\,t^{-5}-40(1-\cos t)t^{-6},$$
$$=t^{-4}\{4+2(1-\cos t)+16\sin t\,.\,t^{-1}-20(\sin\tfrac{1}{2}t/\tfrac{1}{2}t)^2\}.$$

Hence for all values of t

$$|\phi''(t)|\leq 12t^{-4}(4+2+16+20)\leq bt^{-4}, \text{ say,}$$

while, since $$\underset{t\to 0}{\mathrm{Lt}}|\phi''(t)|=1/15,$$

we see that, for $t\leq 2$, $|\phi''(t)|$ is numerically less than a certain corresponding number c. In particular, for values of $r\leq N$, since $X_r<(N+2)h$, we have, provided $h<1/3$, $|\phi''(t)|<c$. Hence

$$|G(h)|\leq\sum_{r=1}^{M} rS_r 2h^2c+\sum_{r=1}^{N} r(S+e)2h^2c+\sum_{r=N+1}^{\infty} r(S+e)2h^2bX_r^{-4}.$$

The first summation on the right has, since M is independent of h, the unique limit zero as $h \to 0$. The second summation is $c(\mathrm{S}+e)\,\mathrm{N}(\mathrm{N}+1)h^2$, and has, therefore, the limit $c(\mathrm{S}+e)$. Finally, since

$$\mathrm{X}_r^{-4} \leqq (r+2)^{-4}h^{-4} < \mathrm{N}^2(r+2)^{-4}h^{-2},$$

the third summation is less than

$$2b(\mathrm{S}+e)\,\mathrm{N}^2\sum_{r=\mathrm{N}+1}^{\infty} r(r+2)^{-4} < 2b(\mathrm{S}+e)\,\mathrm{N}^2\sum_{r=\mathrm{N}+3}^{\infty} r^{-3}$$
$$< 2b(\mathrm{S}+e)\,\mathrm{N}^2\int_{\mathrm{N}}^{\infty} x^{-3}dx < b(\mathrm{S}+e).$$

Hence, finally, $$|\mathrm{G}(h)| \leqq \mathrm{H}+(c+b)(\mathrm{S}+e),$$

where H vanishes with h, for values of h less than $1/3$, and less than $1/\mathrm{M}$, where M depends on e, and e is as small as we please. Thus

$$\mathop{\mathrm{Lt}}_{h\to 0} |\mathrm{G}(h)| \leqq k\mathrm{S},$$

where $k = b+c$ is independent of x.

§ 5. If we next make the hypothesis that a_n and b_n have zero as limit when $n \to \infty$, it at once follows that the series of which $\mathrm{F}(x)$ is the sum converges uniformly, and that accordingly $\mathrm{F}(x)$ is a continuous function. It also follows that, as Riemann has shown,

$$\frac{\mathrm{F}(x+h)-\mathrm{F}(x)}{h} - \frac{\mathrm{F}(x-h)-\mathrm{F}(x)}{h}$$

has zero as unique limit, as $h \to 0$.

Further, as we have already remarked, the upper and lower limits of

$$\mathrm{G}(h) = \{\mathrm{K}(x+h)+\mathrm{K}(x-h)-2\mathrm{K}(x)-h^2\mathrm{F}(x)\}/\tfrac{1}{12}h^4$$

lie between those of

$$\{\mathrm{F}(x+h)+\mathrm{F}(x-h)-2\mathrm{F}(x)\}/h^2.$$

Hence, on the hypothesis stated in the first of the theorems stated in § 1, it follows that, if $f(x)$ be any one of the limits of $\mathrm{G}(h)$, it is one of the limits of the latter expression, and is summable and finite except at the points of a set E which has no perfect sub-set. In fact, by the theorem of § 4 it is numerically less than a function having these properties.

We have therefore only to apply Theorem 7 of de la Vallée Poussin's first paper, above cited, to see that our theorem is true.*

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* Here we may conveniently make use of the theorem that a trigonometrical series is a Fourier series, if its second integrated series converges to a repeated integral. Moreover, the function of which it is the Fourier series is the second differential coefficient of this repeated integral. See W. H. Young, *loc. cit.*

§ 6. Now let us omit the hypothesis that a_n and b_n converge to zero. Then it will no longer be possible to assert *a priori* that the expression

$$\frac{F(x+h)-F(x)}{h}-\frac{F(x-h)-F(x)}{h}$$

approaches zero as $h \to 0$. Thus the reasoning of § 5 will no longer apply. We can no longer indeed assert that $F(x)$ is continuous, unless we suppose, which is the case in the enunciation of our second theorem, that the given trigonometrical series is summable (Ck), where k has some value less than unity. It is then possible, as is shown below, to prove that the series of which $F(x)$ is the sum converges uniformly, so that $F(x)$ is continuous. We are thus able to use de la Vallée Poussin's Theorem 6, and so obtain a proof of the latter of our two main results. In our argument we make the tacit assumption that, if the upper and lower functions (Ck) of a series are finite at an assigned point, the same is true of the upper and lower functions (Ck'), where $k' > k$. Moreover if the former are summable, so are the latter, these being in fact less in absolute value than a numerical multiple of the former.

§ 7. It remains then to show that if the series oscillates boundedly (Ck), and s_n denote the ordinary partial summation of the series, then s_n/n^k is bounded, while the series obtained by dividing each term by the kth power of its place in the series oscillates boundedly when summed in the ordinary manner.*

Denote by S_n the Cesàro partial summation. Then, in the case in which $k = 1$, the required result follows immediately from the equation

$$s_n/n = \{nS_n-(n-1)S_{n-1}\}/n,$$

and the equation

$$\sum_{n=1}^{m} c_n/n = 2\sum_{n=1}^{m-1} S_{n-1}/n(n+1)+S_{m-1}/m+s_m/m.$$

When k is not unity we write

$$\Gamma(k+1)(1-y)^{-k-1}\sum_{n=1}^{\infty} c_n y^n = \sum_{n=1}^{\infty} S_n^{(k)} n^k y^n,$$

whence multiplying both sides by $(1-y)^{k+1}$ and comparing coefficients the second of the results follows.

The first result follows similarly by multiplying both sides by $(1-y)^k$, and using the fact that

$$(1-y)^{-1}\Sigma c_n y_n = \Sigma s_n y^n.$$

§ 8. We have also to obtain a relation between the partial summations

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* From this follows that the first, and therefore the second, of the series in the enunciation of § 4 converges everywhere.

(Ck) and the partial summations (Ck'). For this purpose we have merely to use the equation

$$\Sigma S_n^{(k)} n^{k'} y^n = (1-y)^{k-k'} \Sigma S_n^{(k)} n^k y^n, \qquad (k' > k).$$

Now write $k'-k = p$, and expand on both sides, and equate coefficients of y^n.

Suppose m a fixed number so big that, for $n \geq m$, $|S_n^{(k)}|$ is less than its upper bound as $n \to \infty$, when a suitable small quantity ϵ has been added to the latter. Then, for $n > m$ the limits of the coefficient of y^n on the left, taken in absolute value, are expressible in terms of the limits of the coefficient of y^n on the right-hand side, by means of an inequality. The required result then easily follows. Thus we obtain the result that the upper limit of the modulus of the Cesàro partial summations (Ck') is less than a numerical multiple,* independent of x, of the corresponding upper limit of the modulus of the Cesàro partial summations (Ck). It accordingly follows that, if the Cesàro partial summations (Ck) have the property hypothecated in the second theorem of §1, the Cesàro summations $(C1)$ have the same property. Thus the theorem of §3 is applicable.

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* It is of course not necessary for our purpose here to show that this numerical quantity is unity.

Atomic Specific Heats between the Boiling Points of Liquid Nitrogen and Hydrogen. I.—The Mean Atomic Specific Heats at 50° *Absolute of the Elements a Periodic Function of the Atomic Weights.*

By Prof. Sir JAMES DEWAR, F.R.S.

(Received May 29,—Read June 19,—Revised July 30, 1913.)

A method of determining the specific heat of substances at low temperatures was described in a paper on "Studies with the Liquid Hydrogen and Air Calorimeter,"* also in the abstract of a lecture delivered at the Royal Institution entitled "Liquid Hydrogen Calorimetry,"† where the apparatus then used is illustrated.

Continuing the use of the same method, but with some modification of the apparatus, the investigation has been extended to a large number of inorganic and organic bodies. In this later series of experiments, the measurements of the specific heats of materials by the liquid hydrogen calorimeter were made over a range of temperature from boiling nitrogen to boiling hydrogen, a fall of temperature of some 57° Abs.

Weighed pieces of the material are cooled to the temperature of boiling nitrogen in a quartz cooling vessel of special design. By a simple mechanical device they are then released from this vessel, and drop into liquid hydrogen in the calorimeter below. The resulting volumes of hydrogen evaporated are measured. From this value and a knowledge of the latent heat of the liquid hydrogen and the mass of the substance, the specific heat is calculated as follows:—

If V is volume of hydrogen at N.T.P. evaporated by the fall of 1 grm. of the substance through T degrees above the temperature of boiling hydrogen, and s its specific heat, L being the volume of hydrogen evaporated by 1 calorie, then

$$sT = \frac{V}{L}, \quad \textit{i.e.} \quad s = \frac{V}{TL}.$$

The latent heat of liquid hydrogen is taken as 115 calories, and therefore L = 97·05 c.c.; also in these experiments T is constant ($57^\circ{\cdot}5$) therefore

$$s = V \times 0{\cdot}0001792.$$

Thus the hydrogen volumes measured are reduced to V at N.T.P. and simply multiplied by the constant factor 0·0001792, thereby giving the specific heat.

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* 'Roy. Soc. Proc.,' A, vol. 76, p. 325.

† 'Roy. Inst. Proc.,' 1904, vol. 17, p. 581.

The following examples show the actual volumes of gas dealt with:—

The observations were: hydrogen measured over water at 14° C., barometer 771 mm.; calorimeter alone 8 c.c. per minute. The hydrogen evolved by dropping any material into the calorimeter is all collected during about 15 seconds. The volumes observed are corrected by 2 c.c. due to calorimeter alone.

1 grm. Pb gave 168 c.c.

Frozen drops of normal propyl alcohol: 0·234 grm. gave 219 c.c.; 0·275 grm. gave 254 c.c.

Frozen bullets of acetic acid: 0·352 grm, 282 c.c.; 0·342 grm., 268 c c.

Frozen bullets of benzene: 0·273 grm., 188 c.c.

Tabulated results (factor for correction of gas to N.T.P., 0·9499):—

Substance.	Hydrogen volumes at N T P. from 1 gram.	s.	Apparent values.
Lead	159 ·6	0 ·0286	5 ·92 Atomic specific heat.
n-Propyl alcohol	881 ·2	0 ·1536	9 ·47 Molecular "
	869 ·6	0 ·1559	9 ·36 " "
Acetic acid	754 ·4	0 ·1352	8 12 " "
	737 ·9	0 ·1322	7 44 " "
Benzene	648 ·5	0 ·1161	9 ·07 " "

Applying the correction explained later on for heat absorbed in transit, when the neck of the calorimeter is not cooled with liquid air, the following are the mean results:—

Substance.	s.	Real values.
Lead	0 ·0240	4 ·97 Atomic specific heat.
n-Propyl alcohol	0 ·1300	7 ·80 Molecular "
Acetic acid	0 ·1128	6 ·74 " "
Benzene	0 ·0975	7 ·62 " "

In my earlier paper* the value of the latent heat of hydrogen was taken as 122·92. Five observations were given varying ±5 about this mean value. This was determined on the basis of 0·0291 being accepted as the mean specific heat of lead from 15° C. to 20° Abs. Several Willard Gibbs vapour pressure formulæ, however, calculated from the vapour tensions of liquid hydrogen, give a mean value of 115 for the latent heat of hydrogen, so that the specific heat of lead over this range would seem to be 0·0272. Accepting the value of 115 for the latent heat of hydrogen, the resulting value of the specific heat of lead from 80° Abs. to 20° Abs. is now 0·02399. This is the mean value of a series of nearly 30 observations. The greatest variations from this mean value were 0·0247 and 0·0233, but the majority of the values varied to a much less extent. This is equivalent to an atomic specific heat of 4·965. It may be mentioned that a computation from Nernst and Lindemann's* real specific heats of lead within the same range of temperature gives the mean value 5·18.

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* 'Roy. Soc. Proc.,' A, vol. 76, p. 325.

In the observations with the liquid air calorimeter the specific heats were calculated in each case by direct comparison with lead observed at the same time, as explained in the earlier papers. This is most convenient because liquid air varies in composition on standing, and therefore in the volume evaporated by unit amount of heat.

Liquid Air Calorimetry.

A few results obtained with the form of calorimeter used in 1904 with liquid air may be recorded. They were all reduced by comparison with lead done at the same time, using the value for the specific heat of lead given in the earlier paper, viz., 0·0290 from 195° Abs. to 85° Abs. and 0·0295 from 15° C. to 85° Abs.

Substance.	*s*.	Atomic heats and molecular specific heats.
1. From 195° Abs. to 85° Abs.		
Nickel carbonyl, $Ni(CO)_4$	0·1653	28·22
Iron carbonyl, $Fe(CO)_5$	0·1488	29·17
Nickel	0·0736	4·38
Iron	0·0727	4·06
Para-cyanogen, $(CN)_n$	0·1162	3·02 × *n*
Silver cyanide	0·0680	9·11
Tantalum	0·0280	5·07
2. From 15° C. to 85° Abs.		
Silver cyanide	0·0925	12·38
$(CN)_n$	0·1788	$(4·65)_n$

The values of the molecular specific heat of carbonic oxide by difference are 5·97 from the nickel carbonyl, and 5·02 from the iron carbonyl. The relatively high values of the iron and nickel to that observed between 80° Abs. and 20° Abs. are also noteworthy, viz., 4·06 and 4·33, compared to 0·98 and 1·22.

Some observations were done with liquid nitrogen instead of liquid hydrogen, under the same conditions, in the form of calorimeter now described. They were reduced on the basis of the value 48·9 for the latent heat of nitrogen at its boiling point, as given by Fischer and Alt in 1902. The method of calculation was thus similar to that employed with liquid hydrogen. The values obtained, which are probably a little too high, were as follows:—

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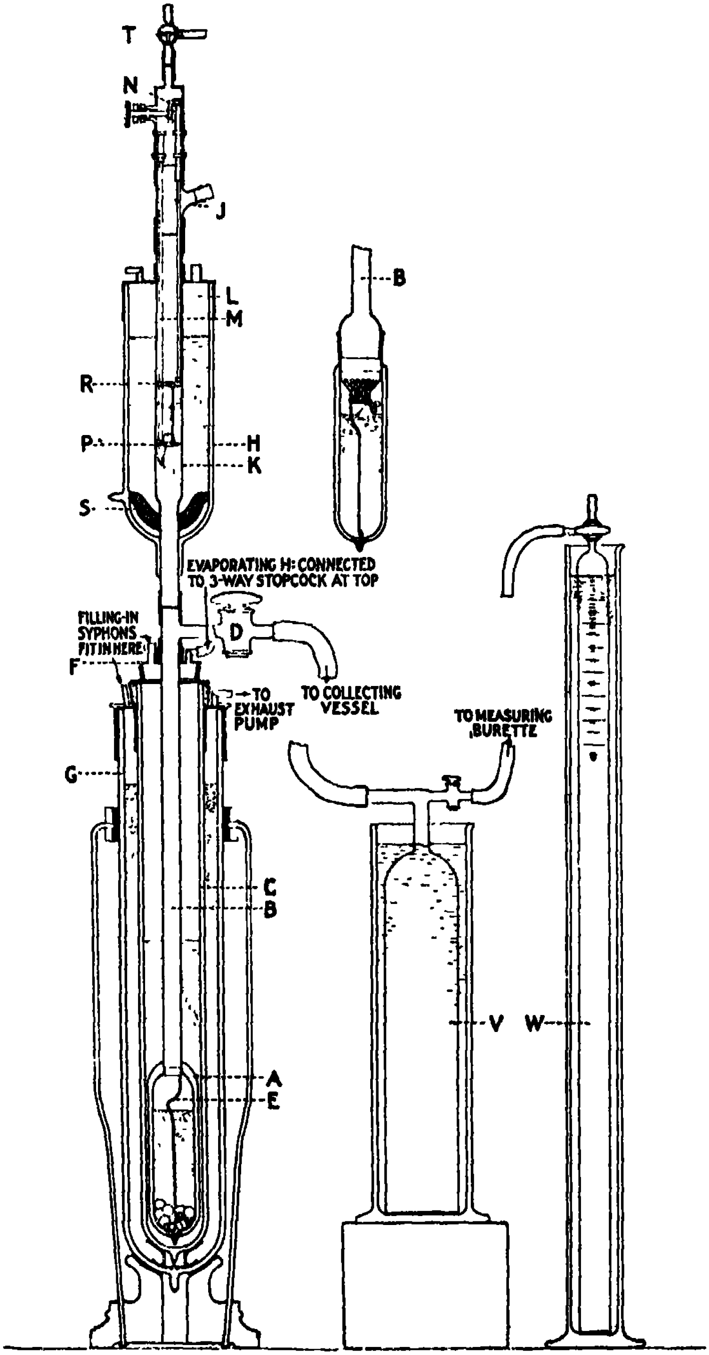
* 'Sitzungsber. d. Berl. Akad.,' 1911, p. 494.

Substance.	s.	Atomic heat.
1. From 15° C. to 77·3° Abs. (B.P. of nitrogen).		
Lead	0·0300	6·21
Bismuth	0·0295	6·14
Thallium	0·0311	6·36
Aluminium	0·1737	4·71
Magnesium	0·2068	5·05
2. From 195° Abs. to 77·3° (solid CO_2 to liquid nitrogen).		
Mercury	0·0313	6·26
Bismuth	0·0291	6·06
Thallium	0·0308	6·30
Aluminium	0·1540	4·17
Magnesium	0·1550	3·78

The liquid hydrogen calorimeter is a glass cylindrical bulb vacuum vessel A (fig. 1) of 50 c.c. capacity, silvered, with ½ cm. slit. The inner diameter is 3 cm. On to the neck, contracted to about 1·7 cm., is sealed a glass tube B of equal diameter and 38 cm. long. This projects about 8 cm. through the brass coned fitting cap F of an ordinary slit silvered vacuum vessel in which it is supported. A side delivery tube, 1 cm. wide, provided with a stopcock D of 8 mm. bore, is sealed near the top of B. A short length of rubber tubing on the neck of F makes a gas-tight joint with B. To minimise splashing, and to reduce the impact of the falling pieces, a thin strip of german silver or lead E, bent out near the top into a shoulder about 1 cm. square, stands centrally in the calorimeter A. The strip is cut from a thin tube of about the same diameter as the calorimeter neck. A short length of the tube is left above the shoulder, and supports the strip by fitting loosely into the neck of A. The shoulder is arranged just above the level of the liquid hydrogen in A, which is at least three-quarters full. Some such device is essential in the use of this form of the liquid hydrogen calorimeter.

The calorimeter in its turn is immersed in liquid hydrogen in the supporting vacuum vessel C, the neck of the calorimeter being 8 to 10 cm. below the liquid hydrogen surface. This vacuum vessel C is only slightly wider than the lower part of A, and is provided with a coned cap F, whereby it is also supported and completely immersed in a wider vacuum


T
N
J
B
L
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R
P
H
K
S
EVAPORATING H: CONNECTED TO 3-WAY STOPCOCK AT TOP
FILLING-IN SYPHONS FIT IN HERE
F
D
TO EXHAUST PUMP
TO COLLECTING VESSEL
TO MEASURING BURETTE
G
C
B
V
W
A
E

Fig. 1.

vessel G containing exhausted liquid air. G is also fitted with a brass coned cover, fitting vacuum-tight on to the cap F on C. Both caps are pierced by two thin tubes, one for fitting on to the filling syphons, the other, bent at right angles, serves for connecting to the exhaust in the case of the liquid air vessel, and in the case of the liquid hydrogen vessel to the stopcock leading the evaporating hydrogen through the upper part of the apparatus.

This arrangement thus charged only needs a little liquid air sucked in every one and a-half hours. The liquid hydrogen vessel will not need replenishing for at least four hours. The level of the liquid hydrogen in the calorimeter does not fall 1 cm. in six hours with constant use. The bulk of the materials added roughly compensates for the volume of the liquid hydrogen evaporated. It is important that this level should not materially change, since, after striking the shoulder, bodies move more slowly, are deflected on to the cold wall, and low results are obtained due to longer cooling of the materials in the vapour before being immersed in the liquid hydrogen.

The isolation of the calorimeter was such that less than 10 c.c. of hydrogen gas was evaporated from it per minute. The whole apparatus is supported between the cork-lined spring jaws mounted on a heavy metal base, on which the outer vacuum vessel rests.

The cooling vessel H is connected by india-rubber tube to the top of the calorimeter. It consists of an ordinary cylindrical slit silvered vacuum vessel, 20 cm. long and 7 cm. wide, with a central axial open tube K sealed in below. This tube passes through the liquid in the vacuum vessel. It has the same diameter below as the neck tube of the calorimeter. Near the top of the central tube a side tube J, of about the same diameter, and some 3 cm. long, serves for the introduction of the weighed pieces of material, which are all cooled previously to the temperature of liquid air, and then fall on to a thin metal disc P fitting loosely the tube K, where they remain about 15 minutes. P is supported by being hinged to two thin ebonite rods, L and M, fixed to a brass fitting cemented on to the top. The rod L is not fixed directly to the disc but to a metal ring R. From the ring R two thin vertical steel wires are connected freely to two points on the circumference of the pan below. This rod and the attached ring can be given a vertical motion by a crank N in the top fitting, thereby tipping the pan and releasing the piece of material, which then falls freely down into the calorimeter. The level of the pan placed about H is approximately one-third the vertical height of the cooling vessel. Quartz was found to be safer than glass for the construction of this vessel. A high vacuum was maintained by a cross-tube S, opening to the annular space, filled with charcoal.

At the temperature of boiling nitrogen, the convection currents in the central tube of such a vessel, when connected to the calorimeter below, have no serious effect on the temperature in the tube at a reasonable distance from the bottom, provided the central tube be not wide. The difference of temperature in the tube and in the surrounding liquid was found to be only 0·5° when the tube was 1·5 cm. wide. With a larger pattern vessel the width of the central tube was increased to 2·2 cm., and even here the difference was under 3° at the level of the pan. These temperatures were measured by a small helium thermometer, consisting of a 4 c.c. bulb to which was sealed a small mercury manometer of fine capillary tubing. The thermometer was filled with pure helium to 273 mm. pressure at 0° C. The reading of the mercury manometer thus gives, with slight corrections previously determined, the absolute temperature. It is scarcely necessary to add that, by exhausting the liquid nitrogen, a lower initial temperature than 78° Abs. can be secured.

The hydrogen evaporating from the liquid in the vacuum vessel C, in which the calorimeter is immersed, is employed in the interval of observations to maintain a hydrogen atmosphere through the neck of the calorimeter and the connected measuring tubes. Risk of solid air in the calorimeter neck is thus obviated. A simple arrangement of a three-way cock T, connected at the top of the brass fitting on the central tube of the cooling vessel, allows this to be manipulated. The hydrogen thus passes continually in at the tubular top of the fitting on the central tube of the cooling vessel, and out through the stopcock on the calorimeter neck, and through the cocks to the measuring vessels. When an observation is to be made, the three-way cock is turned to allow the hydrogen current to escape to the laboratory, thereby closing off the calorimeter, which now only connects to the collecting and measuring vessels V and W.

V consists of a glass tube 8 cm. in diameter and 40 cm. long, open at the bottom and provided with a wide T-piece at the top. The tube is immersed to the neck in water in a glass cylinder, and is counterpoised by a weight and cord running over a pulley just above. It is thereby readily raised during the time gas is being evaporated from the calorimeter; this ensures that no back pressure is produced. One arm of the T-piece is open and connects to the stopcock D on the calorimeter neck; the other is provided with another small stopcock and connects to a 200 c.c. gas burette W similarly immersed in water. This latter stopcock is closed during the collecting of the gas from a dropped piece of material. This being completed, the calorimeter stopcock is closed while the evaporated hydrogen gas is measured by transference to the burette, the slight continual evaporation from the calorimeter meanwhile finding a vent through the three-way cock T at the top of the cooling vessel, which is now turned on. These arrangements are necessary to secure the minimum impediment to the evaporating hydrogen, which is usually evolved in less than 10 seconds, any temporary back pressure being fatal to concordant results. At least 15 seconds are allowed for collecting the gas given off, and even longer, in some cases, with badly conducting bodies.

A slightly different form of calorimeter vacuum vessel was used on some occasions, but without modifying the results. Instead of the constriction at the top of A, a ground conical neck was used of the same diameter as the inner tube. This neck was fitted with a similar ground conical hollow tube sealed on to the tube B. Anhydrous glycerin was used to make the ground joint tight at the low temperatures. The wider neck in some ways simplifies the preliminary manipulations, and allows a more efficient arrangement to be securely fixed for preventing splashing, and breaking the fall of the bodies dropped into the calorimeter. The arrangement is shown in the side sketch B. It consists of a light counterpoised trap door hinged at the lower end of a conical brass or german silver tube, supported in and fitting to the inner tube of the calorimeter. A small lead ball on a wire soldered to the trap door keeps this closed until struck by a falling sphere, while shutting it again immediately after its passage. The conical tube above the trap door is pierced with several small holes to leave a free passage for the evaporating hydrogen. The addition of a gauze filter to intercept spray was found to be impracticable, the resistance introduced causing back pressure.

As far as possible the materials used were cast in the forms of spheres about 8 mm. diameter, and for this purpose the use of an ordinary bullet mould was found convenient. In the case of liquid bodies, the mould was first cooled by liquid air. Frequently liquids were frozen into solid cylinders in thin glass tubing, and pieces cut off after removing the glass mould. The metallic materials were in some cases fused into buttons of convenient weight in an exhausted quartz tube. The lead, however, of which many pieces were required, was cut from rod, and subsequently squeezed in a small spherical mould.

Volatile bodies were weighed at a low temperature on a light german silver pan supported by a thin platinum wire suspension from the balance pan about 2 cm. above the level of liquid air contained in a wide deep vacuum vessel. Some materials would not make coherent bullets or cast sticks. These were filled into very thin walled cylindrical metal capsules of equal weight, so that a preliminary determination of the volume of hydrogen evaporated by the metal of the capsule gave the correction. They were then cooled on an aluminium dish floating on liquid air, filled with the fluid, and weighed separately. Materials which could not be fused were compressed hydraulically into small blocks and cut up into pieces of suitable dimensions.

At least three pieces of every substance were dropped. The results rarely varied among themselves by more than 2 to 3 per cent. Very frequently the agreement was within 1 per cent. In order to ensure good results, uniformity of shape and size in the pieces of material used is desirable, so that the manner of release and fall shall be comparable: because in the use of this instrument the materials have to pass through a region of the neck, between the cooling vessel and the calorimeter, where a considerable gradient of temperature exists. It is necessary that, as far as possible, the bodies used shall be subjected to this variable region in the same manner, so that the amount of heat absorbed in transit shall be nearly the same. This value was determined in the following manner. The warm portion of the calorimeter neck between the cooling vessel above and the vacuum vessels below was cooled by being surrounded with liquid air placed in a simple temporary fitting. Observations with various kinds of bodies were then made. The comparison of the reduced volumes now obtained with the values given by the ordinary use of this particular form of the instrument gives the correction factor. Many confirmations of the specific heats were made with this addition to the instrument. In the latest form of the calorimeter the neck is always surrounded with liquid nitrogen, thus abolishing all heat correction. This improved calorimeter gives results differing but slightly from the corrected values of the old instrument. The value of the atomic heat of lead is determined before and after any series of experiments as a check on the constancy of the instrument.

The values of the specific heats given will include any heat of transformation of glassy or crystalline modifications or other comparable change produced by the cooling to 20° Abs. Another effect is produced by some materials when used in the form of hydraulically compressed blocks. Such as are porous exhibit in varying degrees the phenomenon of heat evolution due to liquid hydrogen passing into the capillary spaces, thereby rendering the observed specific heat too great unless the proper correction is made. Any air occluded during the preliminary cooling of the porous material to liquid air temperature before being introduced to the hydrogen calorimeter is also included. Some of this air would be replaced by hydrogen through diffusion while in the hydrogen atmosphere in the central tube of the cooling vessel of boiling nitrogen; but the true remedy is the preliminary cooling of such porous bodies in a hydrogen atmosphere to the temperature of liquid air. That heat evolution continued in many cases for some time after the dropping of the material was shown by an increased rate of evolution of hydrogen from the calorimeter. As stated above, this is normally less than 10 c.c. per minute. In some instances the introduction of porous material increased this for some time to more than 30 c.c. per minute.

The values set out in Table I for the mean atomic specific heats of 53 elements at about 50° Abs. represent the results of some 200 calorimetric observations. When plotted in terms of their atomic weights, they reveal definitely a periodic variation resembling generally the well-known Lothar Meyer atomic volume curve for the solid state. The relation between the two curves is shown in fig. 2. If experiments were similarly made between the boiling points of hydrogen and helium then in all probability the atomic specific heats would be all very small and nearly constant.

Until more accurate values of the atomic heats have been reached, by the use of purer samples of the elements and the latest form of this calorimeter, it will be advisable to delay theoretical discussion.

The second part of this paper will contain the molecular specific heats of a series of inorganic compounds; while a third part will include similar values derived from the examination of types of organic bodies.

Table I.

Element.	Atomic weight.	Specific heat.	Atomic heat.
Lithium	7·03	0·1924	1·35
Glucinum	9·1	0·0137	0·125
Boron	11·0	0·0212	0·24
Carbon (Acheson graphite)	12·0	0·0137	0·16
Diamond	12·0	0·0028	0·03
Sodium	23·0	0·1519	3·50
Magnesium	24·4	0·0713	1·74
Aluminium	27·1	0·0413	1·12
Silicon, fused, elec. cruc.	28·4	0·0303	0·86
" crystallised	28·4	0·0308	0·77
Phosphorus (yellow)	31·0	0·0774	2·40
" (red)	31·0	0·0431	1·34
Sulphur	32	0·0546	1·75
Chlorine	35·45	0·0967	3·43
Potassium	39·15	0·1280	5·01
Calcium	40·1	0·0714	2·86
Titanium	48·1	0·0205	0·99
Chromium	52·1	0·0142	0·70
Manganese	55	0·0229	1·26
Iron	55·9	0·0175	0·98
Nickel	58·7	0·0208	1·22
Cobalt	59·0	0·0207	1·22
Copper	63·6	0·0245	1·56
Zinc	65·4	0·0384	2·52
Arsenic	75·0	0·0258	1·94
Selenium	79·2	0·0361	2·86
Bromine	79·96	0·0453	3·62
Rubidium	85·1	0·0711	6·05
Strontium, impure	87·6	0·0550	4·82
Zirconium	90·6	0·0262	2·38
Molybdenum	96·0	0·0141	1·36
Ruthenium	101·7	0·0109	1·11
Rhodium	103·0	0·0134	1·38
Palladium	106·5	0·0190	2·03
Silver	107·93	0·0242	2·62
Cadmium	112·4	0·0308	3·46
Tin	119	0·0286	3·41
Antimony	120·2	0·0240	2·89
Iodine	126·97	0·0361	4·59
Tellurium	127·6	0·0288	3·68
Cæsium	132·9	0·0513	6·82
Barium, impure	137·4	0·0350	4·80
Lanthanum	138·9	0·0322	4·60
Cerium	140·25	0·0330	4·64
"Didymium"	142	0·0326	4·63
Tungsten	184	0·0095	1·75
Osmium	191·0	0·0078	1·49
Iridium	193·0	0·0099	1·92
Platinum	194·8	0·0135	2·63
Gold	197·2	0·0160	3·16
Mercury	200	0·0232	4·65
Thallium	204·1	0·0235	4·80
Lead	207	0·0240	4·96
Bismuth	208	0·0218	4·54
Thorium	232·5	0·0197	4·58
Uranium	238·5	0·0138	3·30

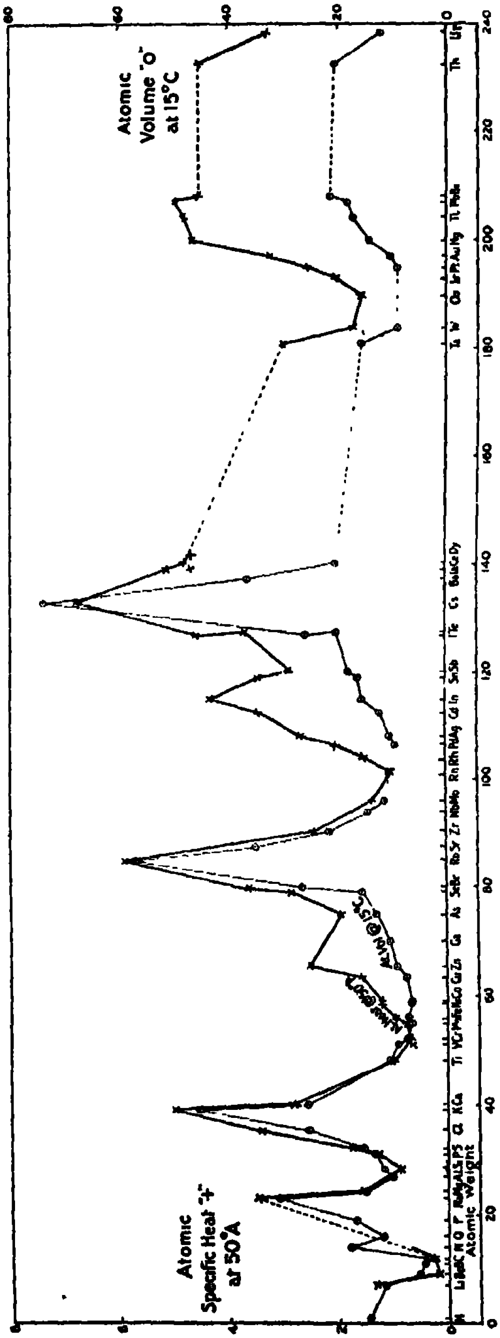

FIG. 2.

During the course of this laborious work Mr. W. J. Green, B.Sc., of the Davy-Faraday Laboratory, has rendered most efficient aid.

The Thermal Effects produced by Heating and Cooling Palladium in Hydrogen.

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(Communicated by Dr. G. T. Beilby, F.R.S. Received June 17,—Read June 26, 1913.)

It is agreed by all observers that a change in the extent to which hydrogen is occluded by palladium takes place at a temperature of about 100° C. This change might be the result of (1) a polymorphic transformation in the metal, or of its surface layer; (2) the formation or dissociation of a compound or solid solution with hydrogen, and, further, the occlusion may be of a dual nature—surface adsorption and diffusion into the metal—these phenomena may take place at different temperatures.

Since the pressure–temperature–concentration relations of hydrogen to palladium have already been the subject of detailed investigations by Hoitsema (1), Roozeboom, and others, and the changes in electrical resistance resulting from occlusion of the gas have been examined by Fischer and Sieverts (2), it appeared advisable to attack the problem from a thermal standpoint, since it has been found that occlusion of hydrogen by the metal is accompanied by an evolution of heat.

This aspect of the question has already been the subject of experiments by Ramsay, Mond, and Shields (3), who argue that if the heat evolution is solely the result of condensation of the gas, the heat evolved during the condensation of equal volumes of hydrogen by different metals should be the same. Calorimetric observations by these authors showed that this was not the case, at any rate for palladium and platinum, the values obtained exhibiting a greater divergence than could be accounted for by experimental error.

The above hypothesis assumes that the gas is condensed in a similar manner by the two metals, but the great difference in the volumes occluded by unit volume of each metal does not, however, support this contention. For example, suppose the gas to be merely condensed on the surface of the one metal either as molecules, or molecular complexes, whilst in the other case it is dissolved in the atomic condition. In both cases a certain amount of heat would be evolved, but in the latter this amount would be diminished by that absorbed in dissociating the gas molecules into atoms, the heat of solution of the gas in this condition not being taken into account.

Little is known concerning the condition of the hydrogen occluded by palladium. From density determinations it appears that the gas is present in a quasi-solid condition, whilst the experiments of Sieverts (2), point to the probability that at temperatures up to the melting point of the metal the gas is dissolved in the atomic state.

Holt, Edgar, and Firth (4) have shown that a close analogy exists between the phenomena of occlusion of hydrogen by palladium, and by charcoal, and according to McBain the gas absorbed by charcoal is present as atoms.

Since any change in the condition of the gas must be accompanied by an evolution or absorption of heat, the study of heating and cooling curves of hydrogen-palladium should afford valuable data, and it is the study of such curves that constitutes the present communication.

Palladium in three different forms was used for the experiments: thin foil (about 0·1 mm. thick), black, prepared by strongly igniting palladium ammonium chloride, and fused metal in the form of a button. The metal was heated in either hydrogen, air, or *in vacuo*, in an electrically heated porcelain tube furnace. The whole apparatus is illustrated in fig. 1. The furnace was so constructed that a vacuum could be maintained on the outside of the heated portion of the tube, in order to give a uniform rate of cooling. The outer jacket consisted of a hard drawn copper tube, to which gunmetal ends were brazed. Between these ends and the porcelain tube were inserted rubber rings, which could be expanded by means of screw caps, thus forming air-tight connections between the tube and outer jacket. The porcelain tube was surrounded by water coolers at both ends. The leads for the heating circuit were passed through air-tight insulators in the outer jacket. Upon

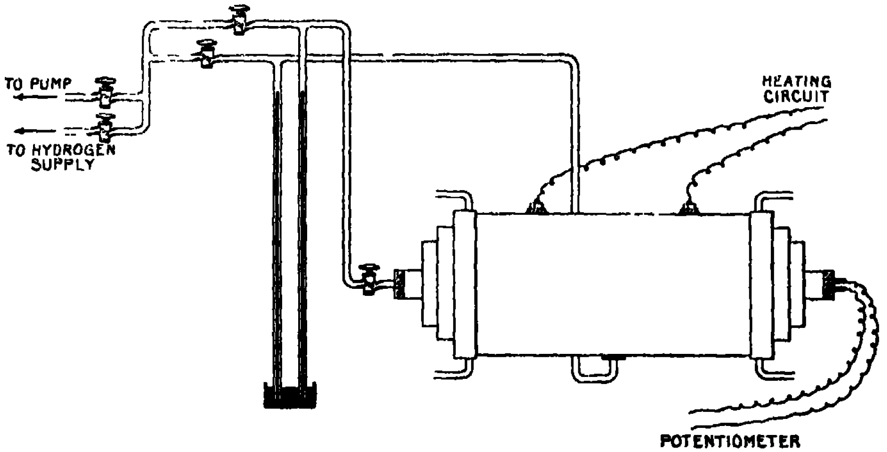

Fig. 1.

evacuating the space between the tube and outer jacket, it was found possible, on account of the vacuum and high reflecting power of the copper, to cool the furnace at a regular and comparatively rapid rate, even at low temperatures. Full details of the furnace are to be found in a previous publication of one of the authors (5).

For detection of thermal changes in the palladium, a platinum-platinum-iridium thermocouple, previously calibrated over the range of temperature concerned, was employed.

In the case of the fused button of palladium, contact was made by inserting the thermocouple into a small hole drilled in the specimen, whilst when using palladium foil or black, the metal was enclosed in a quartz tube and closely packed round the end of the couple, a pad of asbestos keeping the whole in position.

The wires from the thermocouple lying inside the furnace were insulated from each other by means of a two-hole fireclay tube, and passed through a rubber stopper, which made an air-tight joint at one end of the porcelain tube. Outside the stopper they were soldered to copper leads, which in turn were connected through a Carpenter-Stansfield potentiometer to a d'Arsonval mirror galvanometer. The cold junctions were kept at 0° C. by immersing in ice.

The other end of the porcelain tube was connected to a manometer, hydrogen reservoir, and an automatic sprengel pump with three fall tubes, the details of this portion of the apparatus being apparent from the illustration.

The experiments grouped themselves into five categories:—

(i) Heating and cooling the metal *in vacuo.*

(ii) Heating and cooling the metal in hydrogen, after allowing it to occlude gas in the cold, until the initial heat evolution had ceased, and the metal had regained its normal temperature.

(iii) Heating and cooling the metal in hydrogen immediately after the above treatment, and consequently without preliminary occlusion of gas and evolution of heat.

(iv) After cooling in hydrogen and evacuating in the cold, the metal was heated, and the gas still occluded was continuously removed by the pump.

(v) Admitting hydrogen to the metal heated *in vacuo,* and cooling in the gas.

In all experiments the hydrogen was maintained at a constant pressure, slightly higher than that of the atmosphere, in order to prevent inward diffusion of air through the rubber stoppers.

The first series of experiments in which heating and cooling curves of the metal *in vacuo* were taken are illustrated in figs. 2 and 3. In the actual experiments, time readings were taken at constant intervals of temperature, and the differences in time taken to cool, or heat up, through this constant temperature interval, at different temperatures, are plotted against actual temperature readings.

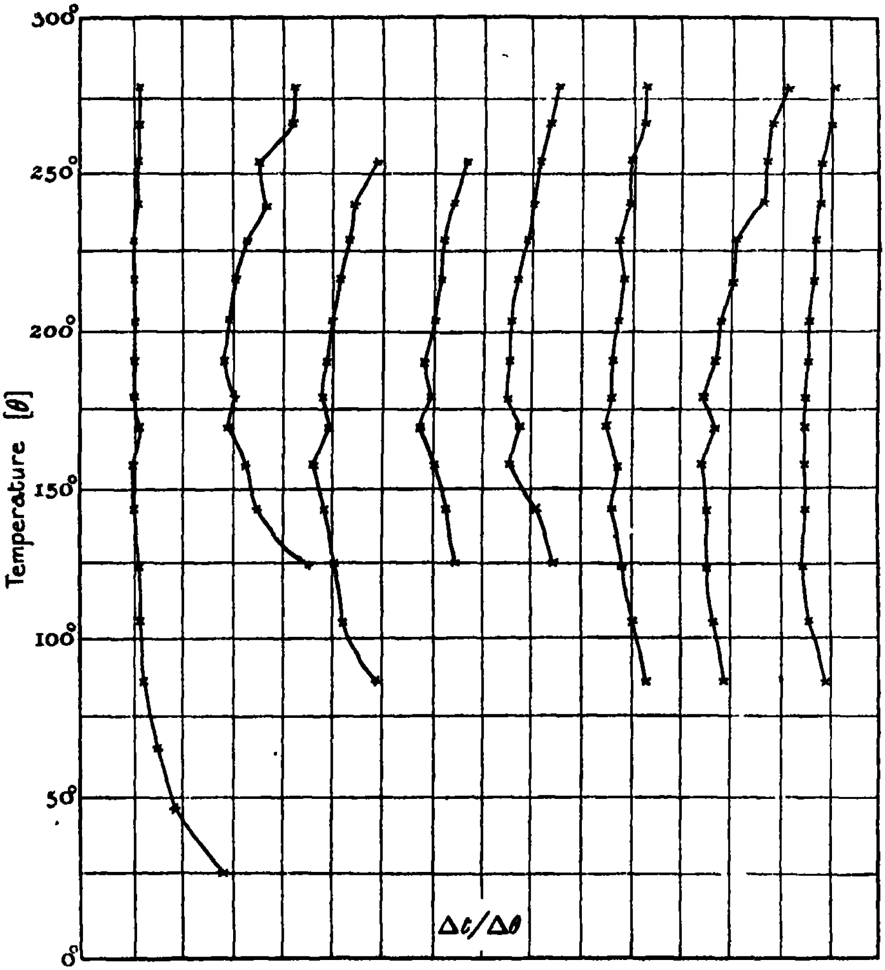

Fig. 2.—Heating Curves of Palladium *in vacuo*.
Nos. 1–7. Palladium foil. No. 8. Palladium black.

The method of plotting is what is generally known as the "inverse rate method," the values of $\Delta t/\Delta\theta$ being plotted against those of θ, where t = time and θ the temperature.

It will be seen from figs. 2 and 3 that, whilst no thermal effect of any magnitude is indicated, small changes in the slope of the curve are apparent at certain temperatures. These might be attributed to experimental error, since they are of very small order, were it not for the fact that the temperature ranges over which they persist are nearly coincident in all the curves. More probably they are an indication of some transformation within the metal, since they represent heat absorption during heating and heat evolution on cooling—complementary effects. If a slow change over a wide range of temperature took place, no great deviation from normal heating and cooling curves would be apparent.

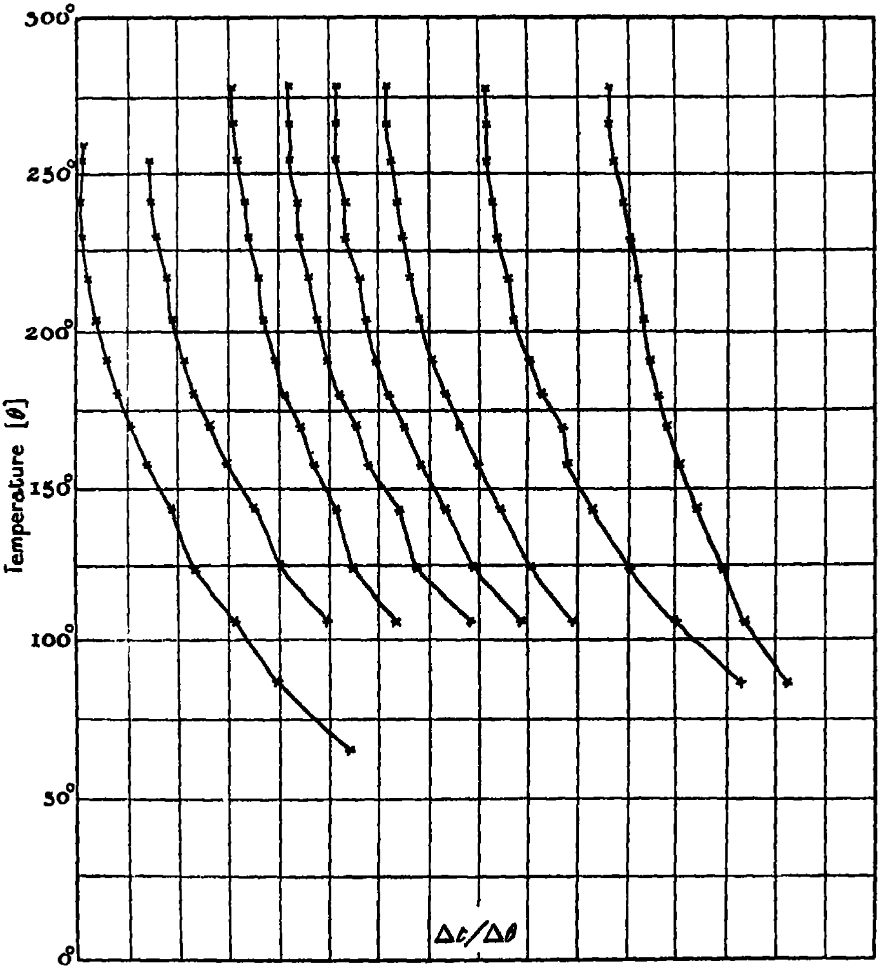

Fig. 3.—Cooling Curves of Palladium *in vacuo*.
Nos. 1–7. Palladium foil. No. 8. Palladium black.

Though the results of the above curves are by no means conclusive, the authors are inclined to believe that they do indicate an allotropic change, and this belief is strengthened by a consideration of the experimental work of other investigators on hydrogen-palladium.

Palladium black, even after an interval of many years, appears always to possess the property of immediately occluding hydrogen, with evolution of heat. A sample of black which had been untouched for over 30 years was found to be in no way different from the freshly prepared substance. If, however, a sample of black be melted into a metallic bead, this property is almost entirely destroyed. Such an inactive bead can, however, always be reactivated by heating to a red heat in air. The probable effect of this treatment is to produce a film of oxide, which in the presence of hydrogen is at once reduced, giving a surface of spongy metal intensely active towards hydrogen. On long standing this property dies away, a phenomenon not observed in the case of palladium black. The reduction of an oxide by hydrogen, or the decomposition by heat of such a compound as ammonium palladium chloride, gives rise to the production of amorphous palladium, which, if uncontaminated by the stable crystalline form, undergoes no change. This would satisfactorily explain the activity of palladium, for whilst the pure amorphous black (which alone appears to possess the property of rapid occlusion of gas) would remain in the meta-stable condition, a film of spongy amorphous metal on a crystalline mass would gradually tend to crystallise, owing to the presence of the stable phase.

A somewhat parallel case is that of grey and white tin. Each variety apart from the other is more or less stable, but if present together in physical contact (as in the case of a mass exhibiting both varieties) the meta-stable passes gradually to the stable form.

It is stated by Ramsay, Mond, and Shields that a unit mass of palladium in any form will occlude the same volume of hydrogen. This occlusion may be, and probably is, an intrinsic property of the metal, but the extreme variation in the rate of initial occlusion of gas, as well as the decay of this rate with time, requires a separate explanation, and the above hypothesis appears to satisfy the experimental observations.

It has been pointed out that palladium black is probably amorphous, since it has been produced by decomposing a compound at a temperature lower than that at which the metal melts, and crystallisation in the case of a metal is usually associated with cooling from the liquid state, and it is this form alone which is able to bring about rapid occlusion of the gas.

It is now usually believed from the work of Beilby (6), Bengough (7), Rosenhain (8), and others, that under certain conditions the crystals of a metal are surrounded by an amorphous metallic cement. Beilby showed that this amorphous material is readily formed upon subjecting the metal to strain, the slipping of the crystals over one another giving rise to its formation. Bengough, however, considers that this amorphous material is present in all metals and alloys, whether they have undergone any mechanical treatment or not. Both, however, consider that this cement ultimately disappears with rise in temperature, the temperature at which it ceases to exist differing in each metal. Rosenhain has carried the matter further still, and quotes experiments to prove the existence of this amorphous cement at all temperatures below the melting point.

If this be the case, it follows from what has been said that palladium cooled from the molten state will contain a minute amount of amorphous matter, and hence should exhibit the power of rapid occlusion of the gas very feebly.

It was found that the activity of palladium in the massive state was considerably affected by first allowing it to occlude gas and then pumping it off; not only was its activity preserved, but it was increased. In the May lecture of the Institute of Metals, 1911, Dr. Beilby makes the following suggestion with regard to the action of gases upon crystallisation. He says: "The gas molecules as they find their way among the metal molecules of the solid are quite capable of producing sufficient movement to arrest crystallisation, or even to flow the crystals which are already formed into the amorphous variety." Dr. Beilby's theory offers a very likely explanation of this increased activity, the continual occlusion and extraction of the gas giving rise to the production of the active amorphous phase.

This view would certainly explain the great changes in the rapidity of the initial occlusion with alteration in the state of the metal. The gas no doubt does subsequently diffuse right into the crystals of the metal, but extremely slowly. A microscopical examination of the surfaces of the palladium before and after saturation with hydrogen exhibited no striking features. In each case the metal was found to be highly crystalline. The surface of the specimen which had been previously saturated with hydrogen had a distinctly pitted structure, dark blotches distributed in an irregular manner throughout the metal being evident. It is quite probable that these dark markings are due to the presence of the amorphous metal formed during the evolution of hydrogen. Palladium black appeared as amorphous grains, with no trace of crystalline structure.

The second series of experiments (in which the metal, after the preliminary heat evolution due to initial occlusion of gas had ceased, was heated and cooled in hydrogen) will next be considered. As has already been mentioned, palladium, in any form except black, will sometimes pick up gas with avidity, and at others with extreme slowness, the heat evolution varying in a parallel manner with the rate of occlusion.

Some measurements of this heat effect have been made, which although by no means accurate, on account of the unsuitability of pyrometric measurements for such determinations, are of interest as showing the great differences which occur. Some values are given in the subjoined table.

Condition of metal.	Temperature before admission of gas.	Rise in temperature after admitting gas.
	°C.	°C.
Black	15	60
Black	310	5
Fused mass...... .	15	3
Fused mass	310	7
Foil (0·1 mm. thick) .	310	3

From these figures, it is evident that, when hot, the heat evolution is practically a constant, no matter what the condition of the metal may be, whereas at the ordinary temperature of the laboratory (about 15° C.) the condition of the metal makes an enormous difference. Hence it may be concluded that when hot the amount of gas picked up by unit mass of metal is constant, and characteristic of the metal, whilst when cold some other influence comes into play. It should be remarked that whilst the heat evolution in the case of the black remains fairly constant (at about 15° C.), with the fused mass it varies somewhat according to the state of its surface.

Determinations were also made to ascertain the heating effect produced by admitting hydrogen to palladium black, at intermediate temperatures between the limits cited. The results are as follows:—

Initial temperature at which hydrogen was admitted.	Rise in temperature.
°C.	°C.
15	53
103	21
120	15
258	8

The rise in temperature, therefore, decreases with the absolute temperature of the metal, as is to be expected from the temperature-concentration relations. The initial heat evolution upon admission of hydrogen is followed by an extremely rapid cooling, more rapid indeed than could be expected from normal cooling, indicating the probability of an endothermic change.

After hydrogen had been admitted to the metal, in the cold, and after any initial thermal effect had died away, the metal was then heated in the gas and heating curves taken. Such curves are shown in fig. 4.

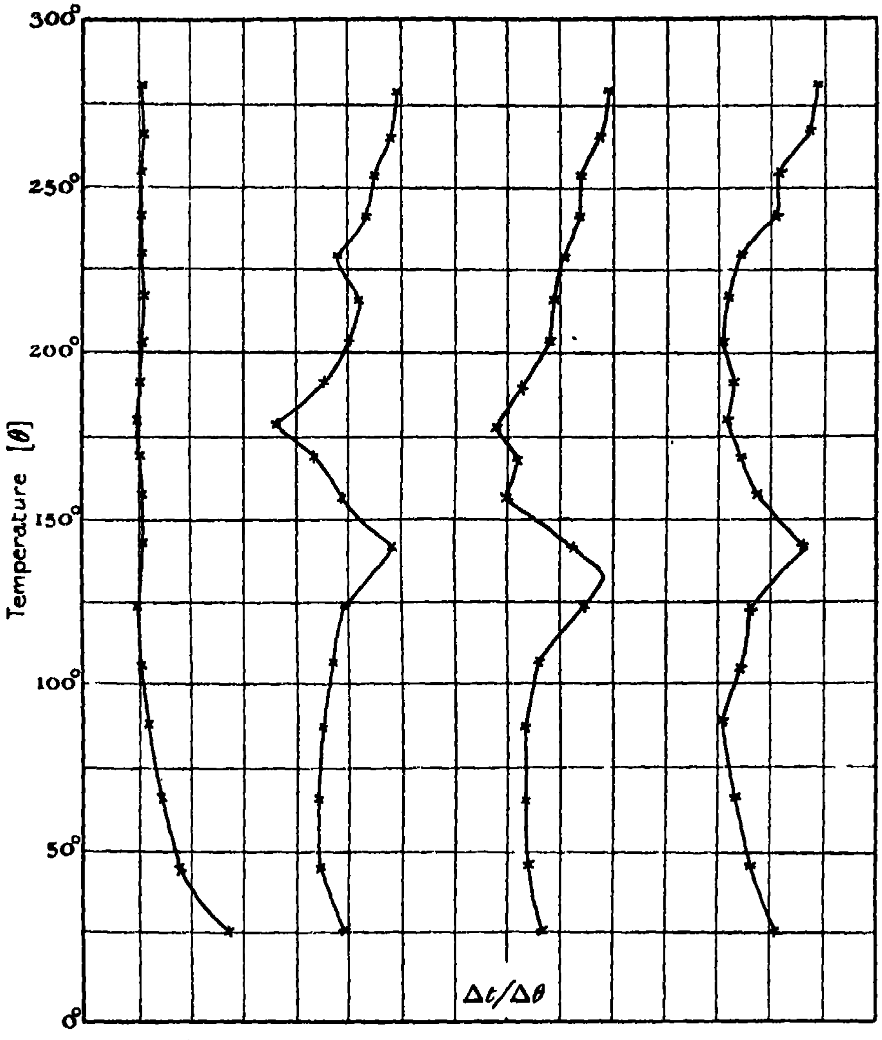

FIG. 4.—Heating Curves of Palladium in Hydrogen.

No. 1. Palladium foil which had evolved no heat upon admitting hydrogen at 15° C.
No. 2. Palladium foil which had evolved heat and occluded hydrogen at 15° C.
No. 3. Palladium black which had evolved heat and occluded hydrogen at 15° C.
No. 4. Palladium button which had evolved heat and occluded hydrogen at 15° C.

These curves can be divided into two classes, according as they do, or do not, exhibit any critical points, and it is remarkable that such points are only shown when there has been initial heat evolution upon admitting gas in the cold. The critical points, whether for black, foil or fused button, all possess a similar character.

An absorption of heat begins at about 95° C., and continues up to a temperature of about 135° C., at which temperature a rapid evolution of heat begins. The absorption of heat between 95° and 135° C. corresponds exactly with the range of temperature over which the great decrease in solubility of the gas in the metal occurs, for at 95° C. (according to Hoitsema's values) about 750 volumes of gas at atmospheric pressure are retained by one volume of the metal, whereas at 135° C. the solubility has decreased to about 100 volumes.

When it is considered that critical changes are only observed when a heat evolution has followed the admission of hydrogen in the cold, and as condensation would cause such a thermal change, an absorption of heat over a temperature range during which most of the occluded gas is being evolved is a natural consequence.

In fig. 5 are shown the cooling curves obtained when the metal after heating in hydrogen was allowed to cool in the gas.

On cooling no prominent points were observed unless the metal had rapidly absorbed gas in the cold and given it off between 95° and 135° C. on heating.

On cooling a heat evolution commences at about 135° and ceases about 105° C., this latter temperature varying somewhat with the condition of the metal. Thus, for palladium black, the heat evolution ceases about 120° C., whilst for palladium foil it ceases about 100° C. It is evident that whatever may be the nature of occlusion, the process is reversible, the evolution of heat on cooling, and absorption of heat on heating, taking place practically over the same temperature, the former heat effect being due to occlusion of gas, and the latter to its evolution. After the metal had completely cooled in hydrogen, it was reheated in the gas. The heating curves are shown in fig. 6.

As might be expected, they are very similar in character to those of fig. 4, but it is remarkable that the temperature of the critical points in the case of palladium foil and fused button varies greatly according to the time the metal has remained in contact with the gas in the cold.

If the re-heating took place almost immediately after the metal had cooled, the point coincided with a temperature of about 140° C., whilst if it had remained a week after cooling the point was raised to about 235° C., and intermediate temperatures were observed for shorter periods of time at room temperature.

In the case of palladium black, this effect was not observed. It would seem, therefore, that when the ratio of surface to mass of metal is not too great, a time limit affects the temperature at which the gas is given off on a somewhat rapid heating, for the point again coincides with rapid evolution of the gas. With very slow heating this difference in temperature is found to be less apparent, so that the effect may be due to a difficulty experienced by the gas in rapidly escaping, otherwise it must be concluded that the

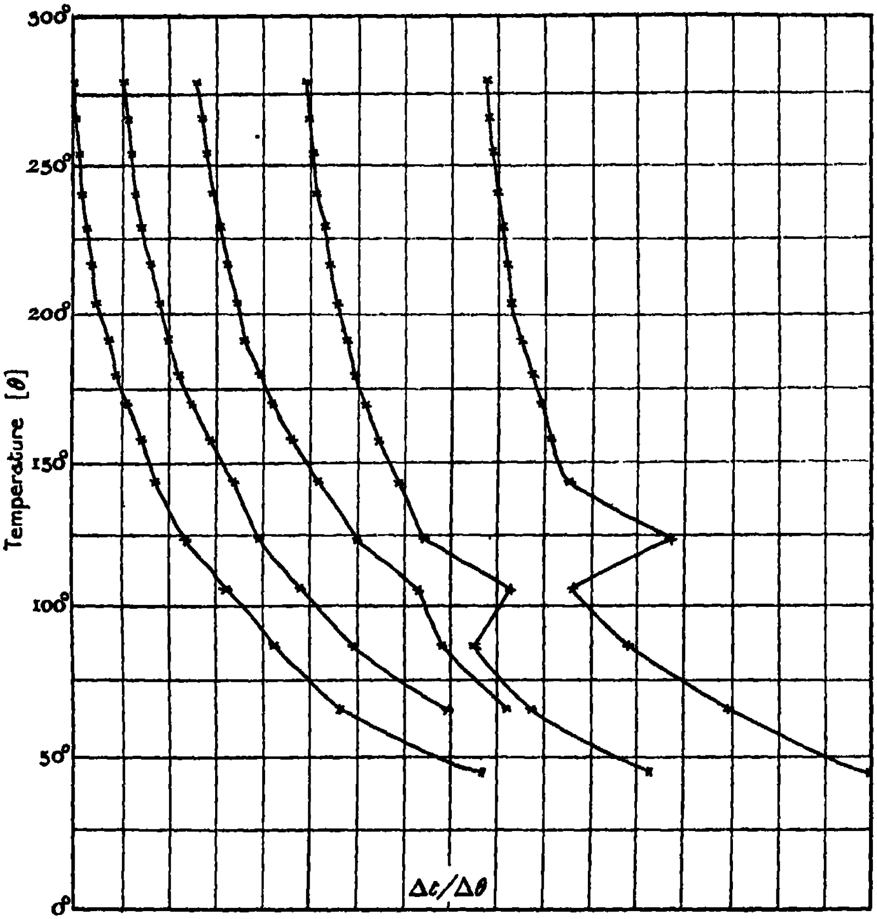

Fig. 5.—Cooling Curves of Palladium in Hydrogen.

No. 1. Palladium button only slightly active towards hydrogen.
No. 2. Palladium foil only slightly active towards hydrogen.
No. 3. Palladium foil more active towards hydrogen than in the case of No. 2.
No. 4. Palladium foil very active towards hydrogen.
No. 5. Palladium black very active towards hydrogen.

Note.—When the palladium button became active, a series of curves similar to Nos. 2, 3, and 4 were obtained.

pressure-concentration values vary with the length of time the metal has remained in contact with hydrogen.

A comparison of these curves with those of fig. 4 shows that, in the case of palladium foil, exactly similar points are observed as in fig. 4. The palladium button, however, gave no point on first heating in hydrogen, and little evolution

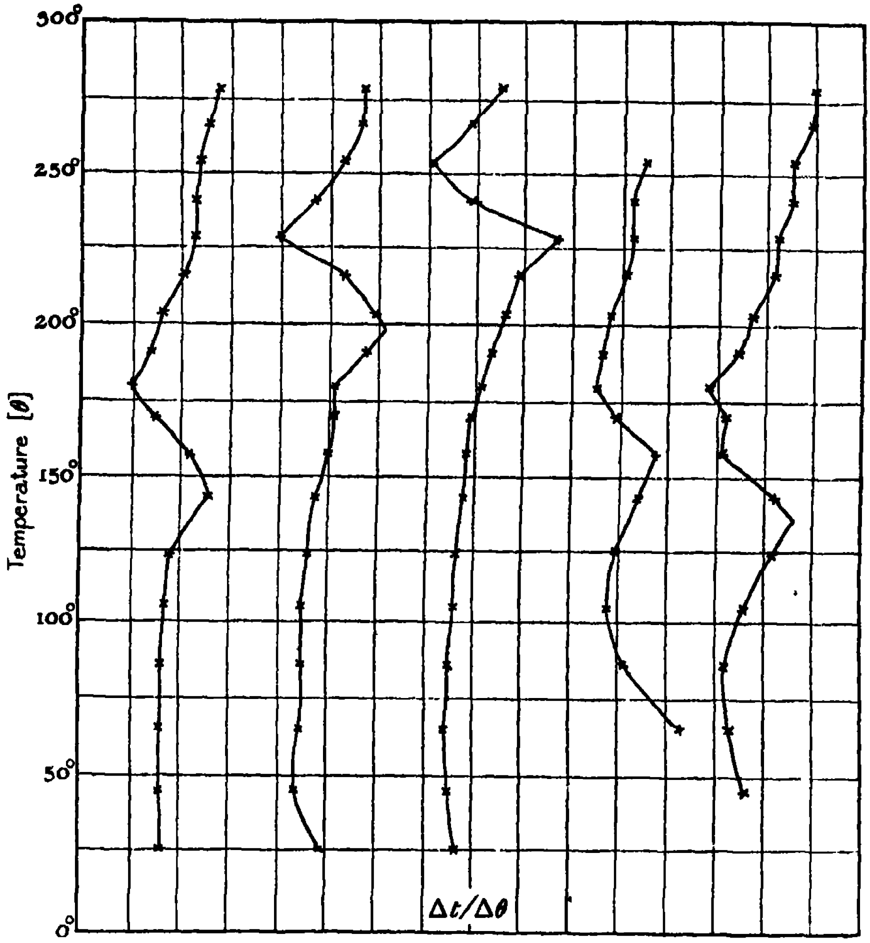

FIG. 6.—Reheating Palladium in Hydrogen.

No. 1. Active palladium foil after remaining 1 hour in hydrogen at 15° C.
No. 2. Active palladium foil after remaining 14 hours in hydrogen at 15° C.
No. 3. Active palladium foil after remaining 8 days in hydrogen at 15° C.
No. 4. Active palladium button after remaining a short time in hydrogen at 15° C.
No. 5. Palladium black The temperature of the critical point being independent of the time of standing in hydrogen.

Note.—A series of curves similar to Nos. 1–3 were also obtained with the palladium button.

of heat was observed upon admitting the gas. A point on cooling indicated, however, that some gas had been picked up.

A further series of curves in hydrogen was taken, but as the results were in every way similar to those already discussed no further comment is necessary. After this second series of curves the procedure was varied.

It was originally observed by Graham, and confirmed by many other observers, that a portion of the occluded gas could be readily pumped off in the cold, whereas part of the hydrogen is held more tenaciously by the metal, and from the experiments of Holt, Edgar and Firth, it is probable that this easily removed portion represents the adsorbed layer, with no doubt some of the inner dissolved gas. When the metal had completely cooled in hydrogen, the surrounding atmosphere of gas, together with this easily removable portion, was pumped off. Heating curves were then taken, the pump meanwhile removing the rest of the gas as it was evolved. The heating curves are shown in fig. 7 and are of considerable interest.

The curves are of four types. In the case of palladium black, it seemed that all the occluded gas could easily be removed in the cold, and hence the heating curves are not characterised by any points. The gas retained by the metal did not exceed ten volumes.

With palladium foil, two distinct types of curves were obtained, according to whether the metal had remained for a long or a short period of time in hydrogen at room temperature.

When it had only remained a short time, about 120 volumes of gas were evolved on heating, or about 0·1 molecule, and the heating curve showed an evolution of heat which attained a maximum at about 190° C.

When, however, it had remained for a long period in contact with the gas, upwards of 890 volumes of hydrogen were found to have been picked up, which is equal to about 0·75 molecule, and the heating curve showed the familiar point at 190° C., a gradual absorption of heat having taken place from about 130° C. The curve is indeed similar to that shown in fig. 6 for palladium after long standing in hydrogen.

It was remarked that, in the case when about 120 volumes of gas were occluded, the gas on heating was evolved at a rate which the pump could easily cope with. When, however, the volume of gas was greater, it was evolved far too rapidly for the pump to remove, and pressures of 200 to 300 mm. were recorded on the manometer. The failure of the pump to remove the gas as fast as it was evolved resulted in a condition similar to that existing in the experiments shown in fig. 6 where the heating was carried out in an atmosphere of hydrogen.

In the case of the fused button, a condition intermediate between these two different cases was observed, a result quite borne out by the heating curves.

It has been shown by Hoitsema, that the portions of the pressure-concentration curves for small concentrations of gas (up to about 0·15 molecule) can be represented by an expression $C/\sqrt{P} = K$, where C is the concentration and P the pressure of the gas, and hence it has been suggested that, at first, the hydrogen is dissolved as atoms. This view is, perhaps, somewhat discounted by the work on absorption of hydrogen by charcoal carried out by

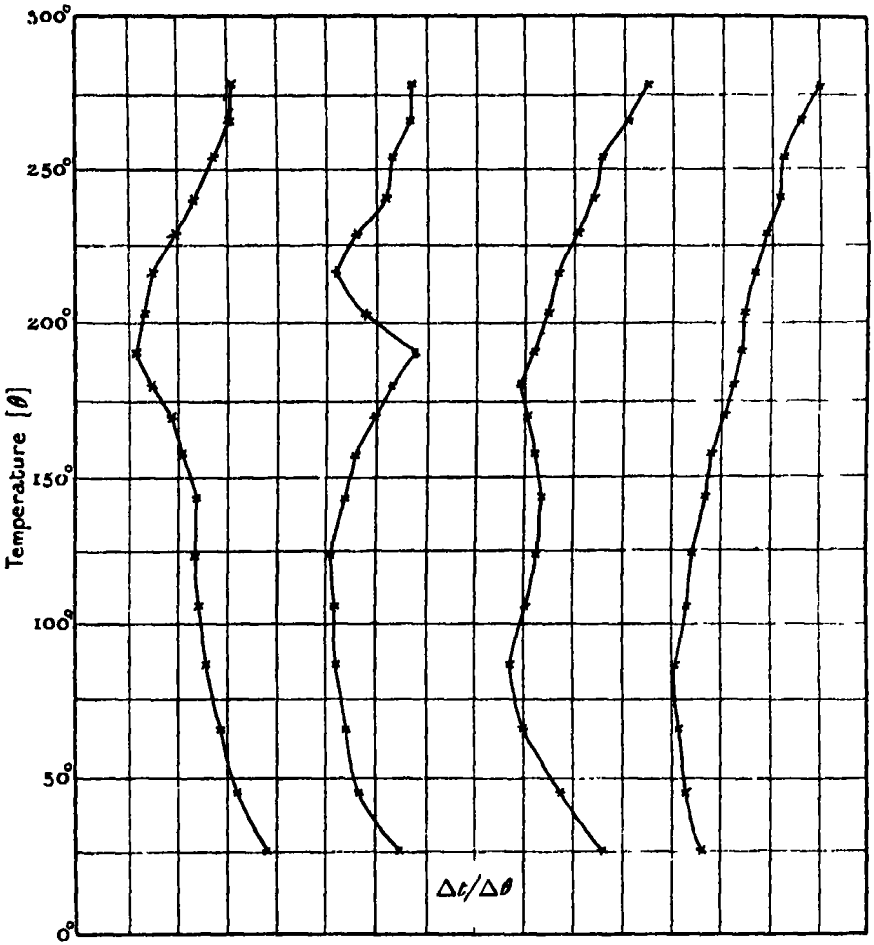

Fig. 7.— Heating Curves of Palladium *in vacuo*.

No. 1. Palladium foil after remaining a short time in hydrogen at 15° C.
No. 2. Palladium foil after remaining a long time in hydrogen at 15° C.
No. 3. Palladium button after remaining a short time in hydrogen at 15° C
No. 4. Palladium black. The time of standing in hydrogen not affecting the curve.

Travers (9), though, on the other hand, it is supported by the work of McBain. It receives distinct confirmation from the heating and cooling curves just described. If the gas was dissolved in atoms, there would be a considerable evolution of heat when it was expelled from the metal, in the ordinary molecular form, and this is precisely what has been observed when only small volumes of gas are pumped out of the metal upon heating. No other simple explanation accounts for an evolution of heat.

Further, above a temperature of about 150° C., the volume of gas retained by the metal does not greatly vary until the melting point is reached, and this volume of gas (about 0·15 molecule) is very rapidly absorbed. It therefore appears probable that it is this gas which one is dealing with in the above experiments, and which causes the almost constant rise of 7° C. when hydrogen is admitted to palladium in the heated state.

In many of the heating curves of palladium in hydrogen, and also palladium *in vacuo*, after cooling in hydrogen, as in case (vi), it is very noticeable that, after the preliminary absorption of heat indicated in the curve by a movement to the right, the curve, instead of returning to its normal position, moves abruptly towards the left. This deflection in the curve can only be interpreted to mean that the initial absorption of heat is followed by an evolution. This phenomenon is exactly the reverse of what takes place at 15° C. upon admitting hydrogen, when, as it has been remarked, the initial heat evolution is followed by a very rapid cooling. This can be explained on the assumption that, whereas the absorption of heat on heating, and evolution of heat upon admitting hydrogen in the cold, are due to condensation of the gas by the amorphous material, the reverse thermal effects are due to the gas either going into or being driven out of solution of the crystalline mass of the metal.

The evolution of heat is most strongly evident in the curves taken after the metal has been in contact with hydrogen for a considerable time at room temperature, which is entirely what would be expected, the absorption of hydrogen by the crystalline particles having had time to take place.

Although the amorphous phase is meta-stable, and must disappear after being some little time in contact with the crystalline variety, its disappearance at 15° C. is not marked by any evolution of gas, all the gas condensed by the amorphous material being absorbed by the crystalline. The amorphous material merely functions, therefore, as a vehicle conveying hydrogen to the mass of metal. Any possibility of it remaining as a stable phase is contrary to phase-rule considerations.

Discussion of Results and Conclusions.

The thermal behaviour of palladium when heated and cooled *in vacuo* furnishes additional evidence of the dimorphic nature of the metal, the stability of the two forms depending upon the temperature. Owing to the stability of the two modifications when existing separately, and the rate of change from one variety to the other being extremely slow, it seems impossible to bring about any rapid transformation, with the result that only a very slight thermal effect is observed upon heating or cooling through the point of transformation.

A consideration of the results of the heating and cooling curves of palladium in hydrogen, and of the relation they bear to the volume of gas evolved or occluded at varying temperatures, also shows that, whatever the nature of occlusion may be, there is every reason to suppose that the metal exists in two different states, depending upon the temperature and mode of treatment.

In the first place, the metal or its surface layer may be brought into a condition which will enable it to occlude large volumes of hydrogen, with evolution of a considerable quantity of heat, at normal temperatures, the magnitude of the heat evolution and volume of initially occluded gas increasing with the ratio of the surface to the mass of metal.

This rapid occlusion of gas by the metal is most probably due to the presence of an amorphous phase.

This portion of the gas which is occluded rapidly is probably present in the metal in the molecular state, or else exists as molecular complexes, for, upon heating, it is evolved with absorption of heat, the complementary effect to that which took place during occlusion.

The same remark applies to the large volume of gas which is slowly picked up by the metal on standing in hydrogen. It is evolved for the greater part with absorption of heat, the evolution of gas taking place at a higher temperature than is the case when the metal is allowed to remain in contact with hydrogen for short periods of time only.

This alteration in the temperature at which it is evolved is probably the result of the gas having more thoroughly penetrated into the interior of the specimen, necessitating, therefore, greater energy to overcome the passive resistance offered by the metal, and cause it to be driven out.

In the absence of an amorphous film on the surface, palladium may be quite passive with regard to rapid occlusion of gas in the cold; it is highly probable, however, that this passivity is apparent rather than real, and that if sufficient time were allowed for occlusion to take place, a volume of gas equal to that occluded by the active material might eventually go into solution.

At temperatures above 100° C., however, whatever may be the condition of the metal (active or passive) a rapid occlusion of a small quantity of hydrogen invariably takes place with the evolution of constant degree of heat. If, after the occlusion of this small amount of gas, the metal is allowed to cool in hydrogen, no critical points present themselves in the cooling curve. If the metal after being allowed to cool in this manner is now heated *in vacuo*, a small evolution of heat is found to occur.

The most feasible explanation of the above phenomena is that, following the initial occlusion of gas molecules, which gives rise to a small evolution of heat, there occurs a splitting up of the molecules into atoms. When this gas is expelled, therefore, an evolution of heat will be indicated, owing to the combination of atoms to form molecules. The cause of the complementary effect not being realised upon admitting the gas to the metal at this temperature is undoubtedly the initial heat evolution, due to adsorption of the gas in the molecular form, and also the fact that the breaking up of the molecules into atoms is not sufficiently spontaneous to give any observable effect.

Hydrogen may be dissolved by both the crystalline and amorphous varieties of the metal, but whilst in presence of the amorphous phase solution of hydrogen is extremely rapid, when this phase is not present solution takes place but slowly. The amorphous phase appears to function as a vehicle for the transference of hydrogen to the crystalline phase.

That temperature is an important factor is quite evident, when it is considered that above a certain temperature all varieties of palladium cease to occlude hydrogen in any quantity. In fact, it may be stated that above 150° C. all forms of the metal have an equal affinity for the gas.

In conclusion the authors wish to express their indebtedness to Prof. Carpenter for the kind interest he has taken, and for the facilities which have enabled them to carry out their investigation.

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Spectroscopic Investigations in Connection with the Active Modification of Nitrogen. III.—Spectra developed by the Tetrachlorides of Silicon and Titanium.

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[PLATE 9.]

Introductory.

In previous papers by Profs. Strutt and Fowler, accounts were given of the spectrum of the afterglow of nitrogen,* and of the spectra of various elements and compounds excited by the nitrogen.† In the course of the latter investigation it was found that carbon compounds introduced into the afterglow developed, in general, the spectrum of cyanogen, the bands, however, undergoing a curious intensity modification as compared with the cyanogen bands produced by the carbon arc in air. The present paper is primarily an account of an investigation which has revealed the interesting fact that tetrachloride of silicon, when brought in contact with active nitrogen, produces a band spectrum of a nitride of silicon, as would be anticipated from the close resemblance of the elements silicon and carbon in their chemical behaviour. An account is also given of experiments on titanium tetrachloride in the afterglow, in which, however, no spectrum attributable to a nitride has been noted.

The method of producing the afterglow was identical with that adopted in former work, and has been described fully by Prof. Strutt.‡

Three spectrographs have been employed: (1) A one-prism quartz instrument giving a linear dispersion varying from 35 to 60 Ångström units per millimetre in the region λ 3900-4900; (2) a Littrow spectrograph giving a dispersion of 9 to 12 Ångström units per millimetre in the same region; (3) a 10-foot concave grating mounted on the plan devised by Eagle,§ and giving 5·5 Å.U. per millimetre in the first order.

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* 'Roy. Soc. Proc.,' 1911, A, vol. 85, p. 377.

† 'Roy. Soc. Proc.,' 1912, A, vol. 86, p. 105.

‡ Bakerian Lecture, 'Roy. Soc. Proc.,' 1911, A, vol. 85, p. 219.

§ 'Astrophys. Journ.,' 1910, vol. 31, p. 120.

Silicon Tetrachloride.

This substance is a colourless, volatile liquid (boiling point 57·5° C.) which fumes in moist air. On introduction of a suitable supply of its vapour, the afterglow became purple in colour. The spectrum was found to consist of—

(1) Unquenched nitrogen afterglow bands.

(2) Silicon lines.

(3) Impurity lines of mercury (λ 2536, 3021, 3023) and bands of cyanogen (heads at λ 3360, 3590, 3883, and 4216, and the associated tails).

(4) A new set of bands in the region λ 3800–4950 attributed to a nitrogen compound of silicon.

The examination of this complex spectrum was facilitated by a comparison with spectrograms of the electric discharge through rarefied vapour of the tetrachloride at a pressure less than its own maximum vapour-pressure, which latter is too high to allow the discharge to pass. The discharge was observed "end-on" through a quartz window, a continuous current of the vapour being maintained throughout the exposure in order to minimise the deposit of solid matter on the window. No trace of the bands attributed to the nitride was detected in this experiment. The line spectrum of silicon was developed very strongly together with flutings probably due to the tetrachloride itself.* Other lines present were due to aluminium (from the electrodes), hydrogen, and chlorine.

The following silicon lines were present in the afterglow. They occurred also in the discharge together with well recognised spark lines

λ (Rowland Scale).	
3905·8	Weaker than in discharge.
3020	Stronger " "
2987·8	Weaker " "
2881·7	
2631·4	Very strong.
2568·8	Very weak.
2532·5	Weaker than in discharge.

---

* The flutings in the discharge attributed to the chloride occur in three clusters :—

(1) Between λ 3066 and 2865, with heads fading off in the direction of diminishing wave-lengths.

(2) Two triple heads, also degraded on the more refrangible side, at λ 2828, 25, 23, and λ 2811·5, 09, 07.

(3) A very strong head at λ 2609·5, fading off towards the red, with fainter heads on either side of it extending from λ 2675 to 2596.

λ (Rowland Scale).	
2528·6	Prominent group, occurring with about the same intensities as in discharge.
2524·2	
2519·3	
2516·2	
2514·4	
2507·0	
2452·2	Prominent group. The first three are weaker than in discharge, while the fourth is very strong.
2443·5	
2438·9	
2435·3	
2219·0	Prominent group, equally well developed in the two sources.
2218·3	
2216·7	
2211·8	
2211·0	
2208·1	

The silicon lines of greater wave-lengths than 3905·8 which occur in the discharge were quite indiscernible in the afterglow. This region in the afterglow spectrum is occupied by the new system of bands. They are degraded towards the red, and the remarkable regularity in their distribution and character will readily be seen in the photographs (Plate 9). Some of the bands exhibit a sudden fall in intensity at a point about four tenth-metres from the head, followed by a recovery in intensity before the final and more gradual fading off. Some heads which are under-exposed might thus easily be mistaken for isolated lines. Other bands have their heads suppressed, the intensity maxima occurring towards the less refrangible portions of the bands. These phenomena have been noted previously in the case of the more refrangible cyanogen bands.

Wave-Lengths of the New Bands.

The positions of the brighter heads were determined from photographs taken with the grating, the comparison spectrum being that of the iron arc. For the fainter bands photographs taken with the quartz spectrograph were utilised, and the limits of error are therefore considerably greater. As many heads as possible were included in the measurements in order to make the discussion of the regularity of structure fairly complete.

In the following table the wave-lengths are given in terms of the International Ångstrom, and the oscillation-frequencies have been reduced to vacuum. The relative intensities have been estimated as nearly as possible on a scale of 10 for the brightest band. The remaining columns refer to the analysis of the bands which follows later :—

Table I.

Wave-length (I. Å).	Intensity	Oscillation frequency (*in vacuo*).	Group	*m*.	*p*.	Observed *minus* calculated.	Remarks.
4947	1	20208	I	14	50	11	
4797	2	20840	II	17	51	−6	
4750	3	21047	II	16	51	−5	
4705 ·9	4	21244	II	15	51	−1	
4665 ·1	5	21430	II	14	51	4	
4629 ·2	3	21596	II	13	51	1	
4618 ·1	2	21648	III	19	52	−1	
4569 ·8	4	21876	III	18	52	−5	
4524 ·3	5	22097	III	17	52	−2	
4482 ·2	6	22304	III	16	52	−1	
4443 ·1	8	22500	III	15	52	1	
4407 ·7	8	22681	III IV	14 20	52 53	1 −3	Two heads superposed.
—	—	[22849]	III	13	52	—	Head undeveloped. Calculated frequency given.
4360 ·4	3	22927	IV	19	53	0	
4345 ·4	2	23006	III	12	52	1	
4317 ·6	5	23155	IV	18	53	−4	
4277 ·0	5	23375	IV	17	53	−2	
4260 ·4	1	23466	V	22	54	4	
4239 ·0	9	23584	IV	16	53	0	
4211 ·9	4	23735	V	21	54	3	
4204 ·0	10	23780	IV	15	53	3	
4172 ·1	6	23962	IV	14	53	4	
4168 ·1	4	23985	V	20	54	−1	
4143 ·0	3	24130	IV	13	53	3	
4126 ·5	8	24227	V	19	54	−3	
4116 ·8	1	24284	IV	12	53	1	
4087 ·3	8	24459	V	18	54	−2	
4050 ·6	8	24681	V	17	54	1	
4032	4	24794	VI	22	55	7	
4016 ·7	6	24889	V	16	54	3	
3989 ·8	4	25057	VI	21	55	−1	
3985 ·8	5	25082	V	15	54	2	
3957 ·7	2	25260	V	14	54	0	
3949 ·8	4	25311	VI	20	55	−1	
3911 ·8	4	25556	VI	19	55	0	
—	—	[25787]	VI	18	55	—	Masked by cyanogen bands (λ 3883 group). Calculated frequencies given.
—	—	[26006]	VI	17	55	—	
3814 ·0	2	26212	VI	16	55	0	

An examination of the frequencies showed that it was possible to arrange them into rows and columns in the manner which has been adopted for the classification of the positive bands of nitrogen, and of the less refrangible cyanogen bands.*

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* Fowler and Shaw, 'Roy. Soc. Proc.,' 1912, A, vol. 86, p. 118.

Table II.

Regularity of the New Bands. Oscillation Frequencies *in vacuo* (larger type); Successive Frequency Intervals (smaller type).

Group...	..VI		V		IV		III		II		I
p..	. 55		54		53		52		51		50
m.											
22	**24794**	1328	**23466**								
	263		269								
21	**25057**	1322	**23735**								
	254		250								
20	**25311**	1326	**23985**	1304	**22681**						
	245		242		246						
19	**25556**	1329	**24227**	1300	**22927**	1279	**21648**				
	231		232		228		228				
18	**[25787]***	1328	**24459**	1304	**23155**	1279	**21876**				
	210		222		220		221				
17	**[26006]***	1325	**24681**	1306	**23375**	1278	**22097**	1257	**20840**		
	206		208		209		207		207		
16	**26212**	1323	**24889**	1305	**23584**	1280	**22304**	1257	**21047**		
			193		196		196		197		
15			**25082**	1302	**23780**	1280	**22500**	1256	**21244**		
			178		182		181		186		
14			**25260**	1298	**23962**	1281	**22681**	1251	**21430**	1222	**20208**
					168		168		166		
13					**24130**	1281	**[22849]†**	1253	**21596**		
					154		157				
12					**24284**	1278	**23006**				

* Masked by CN bands (λ 3883 group).
† Head undeveloped.
The frequencies in the brackets [ ] have been calculated from the formula.

The successive intervals of frequency taken vertically and horizontally form two arithmetical progressions; that is to say, the frequencies in each vertical group may be represented by a formula,

$$n = A' + B\,(m+\mu)^2,$$

and in each row by

$$n = A'' + C\,(p+\pi)^2,$$

where A′, A″, B and C are constants, and successive integral values are given to m and to p, while μ and π are constant fractions. The whole system of bands may therefore be represented by a Deslandres equation,

$$n = A + B\,(m+\mu)^2 + C\,(p+\pi)^2.$$

For the bands observed m takes the integers from 50 to 55, and p ranges from 12 to 22. The more accurately observed frequencies have been utilised in evaluating the constants, and the resulting equation is

$$n = 12{\cdot}10\,(p+0{\cdot}31)^2 - 6{\cdot}27\,(m-0{\cdot}06)^2 - 9211.$$

The degree of approximation to which this formula represents all the bands can be seen from the column in Table I, headed "Observed *minus* Calculated."

Evidence as to the Origin of the New Bands.

The new afterglow bands are not present in the discharge spectrum, in which the chloride is characterised by entirely different bands (see footnote, p. 188). It is probable, therefore, that the new bands are not due to a chloride, but to a nitrogen compound. In the afterglow reaction, chlorine is liberated from the tetrachloride. Prof. Strutt has tested qualitatively the white solid which was deposited on the inside of the afterglow tube in these experiments. The deposit was put in caustic potash solution, and a small quantity of liquid distilled off; this gave a strong Nessler reaction, while blank tests with the potash solution alone gave negative results. This proof of the presence of nitrogen in the deposit confirms the spectroscopic evidence of the nitride origin of the new bands.

It may be recalled that Weiss and Engelhardt* have described the formation of a nitride, having the approximate formula Si_3N_4, by heating silicon in nitrogen at 1300–1400° C. They have also prepared, by other means, another compound, Si_2N_3, which, when ignited and washed with hydrochloric acid, gives rise to a white nitride, SiN. It is impossible to say what is the composition of the nitride giving the band spectrum until a quantitative analysis of the deposit has been undertaken.

Titanium Tetrachloride.

In view of the chemical relations of titanium to carbon and silicon, and especially of the fact that metallic titanium unites very readily with nitrogen forming a nitride, it was thought that titanium tetrachloride might behave in a similar manner to silicon tetrachloride and the carbon compounds in the afterglow.

The tetrachloride of titanium closely resembles that of silicon, being a colourless, volatile liquid (boiling point 136° C.), fuming even more strongly on exposure to the atmosphere. On introduction of its vapour into the active nitrogen, the afterglow became very pale blue in colour. The spectrum was compared with those of titanium oxide in the carbon arc, and of the condensed discharge through the tetrachloride vapour itself, at a pressure less than that of its saturated vapour. The afterglow gives a well developed line spectrum of titanium, with intensities about equal to those in the arc. In addition, and in common with the discharge, it shows the group

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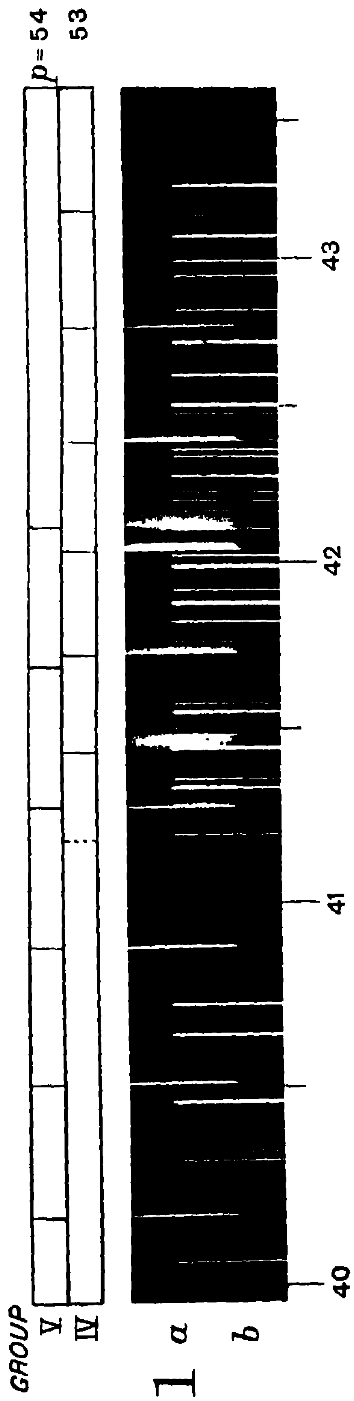
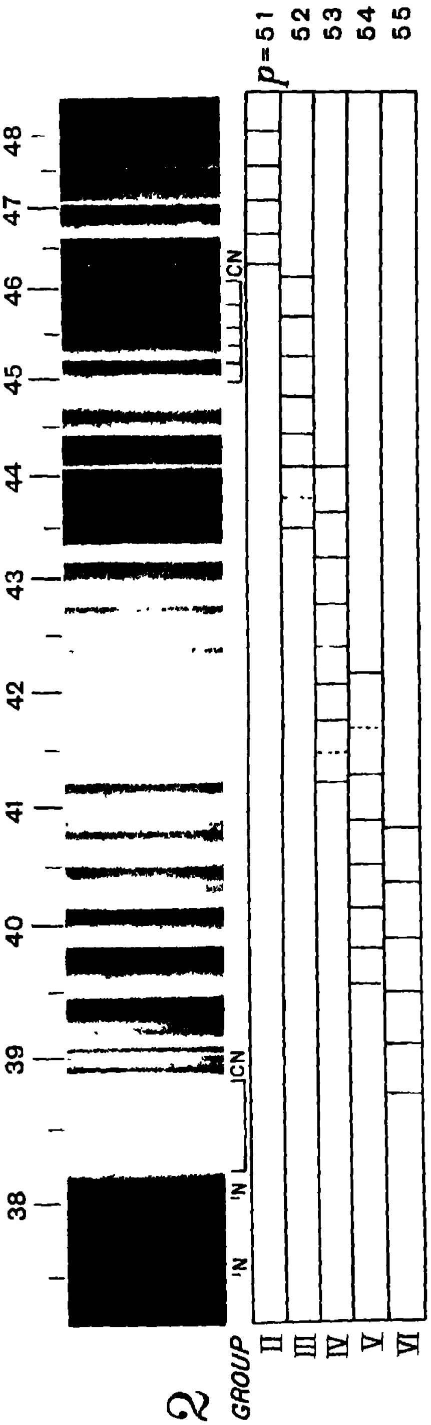
* 'Zeit. Anorg. Chem.,' 1909, vol. 65, p. 38.



1



2

BAND SPECTRUM OF A NITRIDE OF SILICON

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of bands due to the tetrachloride,* with three principal heads, at λ 4199·5, 4192·7, and 4188·0. The enhanced lines of titanium, generally speaking, are not developed in the afterglow, the few which do occur being fainter than in the arc. The condensed discharge through the vapour of the tetrachloride, on the other hand, is noteworthy as being an excellent source of the enhanced lines.

No bands occur in the afterglow which can be attributed to a nitride, although it has previously been proved that nitrogen is present in the compound which is deposited in the apparatus.†

Unlike the carbon compounds and silicon tetrachloride, therefore, the tetrachloride of titanium belongs to the class of substances which, when introduced into the afterglow, do not develop the spectrum of the final product of the reaction.

Summary.

1. The paper gives an account of the spectra developed on the introduction of the vapours of $SiCl_4$ and $TiCl_4$ into the nitrogen afterglow.

2. The $SiCl_4$ afterglow is notable for the occurrence of a new system of bands between λ 3800 and 4950, with heads degraded towards the red. The bands show intensity minima near the heads, corresponding to the modifications of the cyanogen afterglow bands.

3. The wave-lengths of the heads have been determined and their frequencies have been arranged into groups, similar to the classification of the cyanogen bands and the positive bands of nitrogen.

4. The new bands do not occur in the discharge through $SiCl_4$ (which is characterised by a different system of bands) and are therefore attributed to a nitride of silicon. Chemical evidence in support of this has been obtained by Prof. Strutt.

5. The $TiCl_4$ afterglow, however, develops no bands of a corresponding nitrogen compound of titanium. Its spectrum is merely that of the titanium arc, together with the group of flutings characteristic of $TiCl_4$.

I am anxious, in conclusion, to acknowledge my great indebtedness to Prof. A. Fowler, F.R.S., for his valuable assistance throughout this research, and to Prof. the Hon. R. J. Strutt, F.R.S., for the apparatus which he placed at my disposal, and without which the task would have been impossible.

DESCRIPTION OF PLATE.

1. (*a*) Two groups of the bands attributed to a nitride of silicon. (*b*) Iron comparison.
2. Smaller dispersion photograph showing nearly the whole system of nitride bands.

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* Fowler, 'Roy. Soc. Proc.,' 1907, A, vol. 79, p. 509.

† R. J. Strutt, 'Roy. Soc. Proc.,' vol. 88, p. 544.

On the Passage of Waves through Fine Slits in Thin Opaque Screens.

By Lord Rayleigh, O.M., F.R.S.

(Received June 20,—Read June 26, 1913.)

In a former paper* I gave solutions applicable to the passage of light through very narrow slits in infinitely thin perfectly opaque screens, for the two principal cases where the polarisation is either parallel or perpendicular to the length of the slit. It appeared that if the width ($2b$) of the slit is very small in comparison with the wave-length (λ), there is a much more free passage when the electric vector is perpendicular to the slit than when it is parallel to the slit, so that unpolarised light incident upon the screen will, after passage, appear polarised in the former manner. This conclusion is in accordance with the observations of Fizeau† upon the very narrowest slits. Fizeau found, however, that somewhat wider slits (scratches upon silvered glass) gave the opposite polarisation; and I have long wished to extend the calculations to slits of width comparable with λ. The subject has also a practical interest in connection with observations upon the Zeeman effect.‡

The analysis appropriate to problems of this sort would appear to be by use of elliptic co-ordinates; but I have not seen my way to a solution on these lines, which would, in any case, be rather complicated. In default of such a solution, I have fallen back upon the approximate methods of my former paper. Apart from the intended application, some of the problems which present themselves have an interest of their own. It will be convenient to repeat the general argument almost in the words formerly employed.

Plane waves of simple type impinge upon a parallel screen. The screen is supposed to be infinitely thin and to be perforated by some kind of aperture. Ultimately, one or both dimensions of the aperture will be regarded as small, or, at any rate, as not large, in comparison with the wave-length (λ); and the investigation commences by adapting to the present purpose known solutions concerning the flow of incompressible fluids.

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* "On the Passage of Waves through Apertures in Plane Screens and Allied Problems," 'Phil. Mag.,' 1897, vol. 43, p. 259; 'Scientific Papers,' vol. 4, p. 283.

† 'Annales de Chimie,' 1861, vol. 63, p. 385; Mascart's 'Traité d'Optique,' § 645. See also 'Phil. Mag.,' 1907, vol. 14, p. 350; 'Scientific Papers,' vol. 5, p. 417.

‡ Zeeman, 'Amsterdam Proceedings,' October, 1912.

The functions that we require may be regarded as velocity-potentials ϕ, satisfying

$$d^2\phi/dt^2 = V\nabla^2\phi, \tag{1}$$

where $$\nabla^2 = d^2/dx^2+d^2/dy^2+d^2/dz^2,$$

and V is the velocity of propagation. If we assume that the vibration is everywhere proportional to e^{int}, (1) becomes

$$(\nabla^2+k^2)\,\phi = 0, \tag{2}$$

where $$k = n/V = 2\pi/\lambda. \tag{3}$$

It will conduce to brevity if we suppress the factor e^{int}. On this understanding the equation of waves travelling parallel to x in the positive direction, and accordingly incident upon the negative side of the screen situated at $x = 0$, is

$$\phi = e^{-ikx}. \tag{4}$$

When the solution is complete, the factor e^{int} is to be restored, and the imaginary part of the solution is to be rejected. The realised expression for the incident waves will therefore be

$$\phi = \cos(nt-kx). \tag{5}$$

There are two cases to be considered corresponding to two alternative boundary conditions. In the first (i) $d\phi/dn = 0$ over the unperforated part of the screen, and in the second (ii) $\phi = 0$. In case (i) dn is drawn outwards normally, and if we take the axis of z parallel to the length of the slit, ϕ will represent the magnetic component parallel to z, usually denoted by c, so that this case refers to vibrations for which the electric vector is perpendicular to the slit. In the second case (ii) ϕ is to be identified with the component parallel to z of the electric vector R, which vanishes upon the walls, regarded as perfectly conducting. We proceed with the further consideration of case (i).

If the screen be complete, the reflected waves under condition (i) have the expression $\phi = e^{ikx}$. Let us divide the actual solution into two parts, χ and ψ; the first, the solution which would obtain were the screen complete; the second, the alteration required to take account of the aperture; and let us distinguish by the suffixes m and p the values applicable upon the negative (*minus*), and upon the positive side of the screen. In the present case we have

$$\chi_m = e^{-ikx}+e^{ikx}, \qquad \chi_p = 0. \tag{6}$$

This χ-solution makes $d\chi_m/dn = 0$, $d\chi_p/dn = 0$ over the whole plane $x = 0$, and over the same plane $\chi_m = 2$, $\chi_p = 0$.

For the supplementary solution, distinguished in like manner upon the two sides, we have

$$\psi_m = \iint \Psi_m \frac{e^{-ikr}}{r}\, dS, \qquad \psi_p = \iint \Psi_p \frac{e^{-ikr}}{r}\, dS, \tag{7}$$

where r denotes the distance of the point at which ψ is to be estimated from the element dS of the aperture, and the integration is extended over the whole of the area of aperture. Whatever functions of position Ψ_m, Ψ_p may be, these values on the two sides satisfy (2), and (as is evident from symmetry) they make $d\psi_m/dn$, $d\psi_p/dn$ vanish over the wall, viz., the unperforated part of the screen, so that the required condition over the wall for the complete solution is already satisfied. It remains to consider the further conditions that ϕ and $d\phi/dx$ shall be continuous across the *aperture*. These conditions require that on the aperture

$$2 + \psi_m = \psi_p, \qquad d\psi_m/dx = d\psi_p/dx. \tag{8}$$ [*]

The second is satisfied if $\Psi_p = -\Psi_m$; so that

$$\psi_m = \iint \Psi_m \frac{e^{-ikr}}{r}\, dS, \qquad \psi_p = -\iint \Psi_m \frac{e^{-ikr}}{r}\, dS, \tag{9}$$

making the values of ψ_m, ψ_p equal and opposite at all corresponding points, viz., points which are images of one another in the plane $x = 0$. In order further to satisfy the first condition, it suffices that over the area of aperture

$$\psi_m = -1, \qquad \psi_p = 1, \tag{10}$$

and the remainder of the problem consists in so determining Ψ_m that this shall be the case.

It should be remarked that Ψ in (9) is closely connected with the normal velocity at dS. In general,

$$\frac{d\psi}{dx} = \iint \Psi \frac{d}{dx}\left(\frac{e^{-ikr}}{r}\right) dS. \tag{11}$$

At a point (x) infinitely close to the surface, only the neighbouring elements contribute to the integral, and the factor e^{-ikr} may be omitted. Thus

$$\frac{d\psi}{dx} = -\iint \Psi \frac{x}{r^3}\, dS = -2\pi x \int_x^\infty \Psi \frac{r\,dr}{r^3} = -2\pi\Psi; \quad \text{or} \quad \Psi = -\frac{1}{2\pi}\frac{d\psi}{dn}, \tag{12}$$

$d\psi/dn$ being the normal velocity at the point of the surface in question.

In the original paper these results were applied to an aperture, especially of elliptical form, whose dimensions are small in comparison with λ. For our present purpose we may pass this over and proceed at once to consider the case where the aperture is an infinitely long slit with parallel edges, whose width is small, or at the most comparable with λ.

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[*] The use of dx implies that the variation is in a fixed direction, while dn may be supposed to be drawn outwards from the screen in both cases.

The velocity-potential of a point-source, viz., e^{-ikr}/r, is now to be replaced by that of a linear source, and this, in general, is much more complicated. If we denote it by $\mathrm{D}(kr)$, r being the distance from the line of the point where the potential is required, the expressions are*

$$\begin{aligned}\mathrm{D}(kr) &= -\left(\frac{\pi}{2ikr}\right)^{\frac{1}{2}} e^{-ikr}\left\{1-\frac{1^2}{1\,.\,8ikr}+\frac{1^2\,.\,3^2}{1\,.\,2\,.\,(8ikr)^2}-\ldots\right\}\\ &= \left(\gamma+\log\frac{ikr}{2}\right)\left\{1-\frac{k^2r^2}{2^2}+\frac{k^4r^4}{2^2\,.\,4^2}-\ldots\right\}\\ &\qquad+\frac{k^2r^2}{2^2}\mathrm{S}_1-\frac{k^4r^4}{2^2\,.\,4^2}\mathrm{S}_2+\frac{k^6r^6}{2^2\,.\,4^2\,.\,6^2}\mathrm{S}_3-\ldots,\end{aligned} \tag{13}$$

where γ is Euler's constant (0·577215), and

$$\mathrm{S}_m = 1+\tfrac{1}{2}+\tfrac{1}{3}+\ldots+1/m. \tag{14}$$

Of these the first is "semi-convergent" and is applicable when kr is large; the second is fully convergent and gives the form of the function when kr is moderate. The function D may be regarded as being derived from e^{-ikr}/r by integration over an infinitely long and infinitely narrow strip of the surface S.

As the present problem is only a particular case, equations (6) and (10) remain valid, while (9) may be written in the form

$$\psi_m = \int \Psi_m \mathrm{D}(kr)\,dy, \qquad \psi_p = -\int \Psi_m \mathrm{D}(kr)\,dy, \tag{15}$$

the integrations extending over the width of the slit from $y = -b$ to $y = +b$. It remains to determine Ψ_m, so that on the aperture $\psi_m = -1$, $\psi_p = +1$.

At a sufficient distance from the slit, supposed for the moment to be very narrow, $\mathrm{D}(kr)$ may be removed from under the integral sign and also be replaced by its limiting form given in (13). Thus

$$\psi_m = -\left(\frac{\pi}{2ikr}\right)^{\frac{1}{2}} e^{-ikr}\int \Psi_m dy. \tag{16}$$

If the slit be not very narrow, the partial waves arising at different parts of the width will arrive in various phases, of which due account must be taken. The disturbance is no longer circularly symmetrical as in (16). But if, as is usual in observations with the microscope, we restrict ourselves to the direction of original propagation, equality of phase obtains, and (16) remains applicable even in the case of a wide slit. It only remains to determine Ψ_m as a function of y, so that for all points upon the aperture

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* See 'Theory of Sound,' § 341.

$$\int_{-b}^{+b} \Psi_m D(kr)\, dy = -1, \tag{17}$$

where, since kr is supposed moderate throughout, the second form in (13) may be employed.

Before proceeding further it may be well to exhibit the solution, as formerly given, for the case of a very narrow slit. Interpreting ϕ as the velocity-potential of aerial vibrations and having regard to the known solution for the flow of incompressible fluid through a slit in an infinite plane wall, we may infer that Ψ_m will be of the form $A(b^2-y^2)^{-\frac{1}{2}}$, where A is some constant. Thus (17) becomes

$$A\left[(\gamma + \log \tfrac{1}{2} ik)\pi + \int_{-b}^{+b} \frac{\log r \,.\, dy}{\sqrt{(b^2-y^2)}}\right] = -1. \tag{18}$$

In this equation the first part is obviously independent of the position of the point chosen, and if the form of Ψ_m has been rightly taken the second integral must also be independent of it. If its co-ordinate be η, lying between $\pm b$,

$$\int_{-b}^{+b} \frac{\log r \,.\, dy}{\sqrt{(b^2-y^2)}} = \int_{-b}^{\eta} \frac{\log(\eta - y)\, dy}{\sqrt{(b^2-y^2)}} + \int_{\eta}^{b} \frac{\log(y-\eta)\, dy}{\sqrt{(b^2-y^2)}} \tag{19}$$

must be independent of η. To this we shall presently return; but merely to determine A in (18) it suffices to consider the particular case of $\eta = 0$. Here

$$\int_{-b}^{+b} \frac{\log r \,.\, dy}{\sqrt{(b^2-y^2)}} = 2\int_{0}^{b} \frac{\log y \,.\, dy}{\sqrt{(b^2-y^2)}} = 2\int_{0}^{\frac{1}{2}\pi} \log(b\cos\theta)\, d\theta = \pi \log(\tfrac{1}{2}b).$$

Thus $\quad A(\gamma + \log \tfrac{1}{4} ikb)\pi = -1, \quad$ and $\quad \int_{-b}^{+b} \Psi_m dy = \pi A$:

so that (16) becomes

$$\psi_m = \frac{e^{-ikr}}{\gamma + \log(\frac{1}{4} ikb)} \left(\frac{\pi}{2ikr}\right)^{\frac{1}{2}}. \tag{20}$$

From this, ψ_p is derived by simply prefixing a negative sign.

The realised solution is obtained from (20) by omitting the imaginary part after introduction of the suppressed factor e^{int}. If the imaginary part of $\log(\frac{1}{4} ikb)$ be neglected, the result is

$$\psi_m = \left(\frac{\pi}{2kr}\right)^{\frac{1}{2}} \frac{\cos(nt - kr - \frac{1}{4}\pi)}{\gamma + \log(\frac{1}{4} kb)}, \tag{21}$$

corresponding to

$$\chi_m = 2\cos nt \cos kx. \tag{22}$$

Perhaps the most remarkable feature of the solution is the very limited dependence of the transmitted vibration on the *width* ($2b$) of the aperture.

We will now verify that (19) is independent of the special value of η. Writing $y = b\cos\theta$, $\eta = b\cos\alpha$, we have

$$\int_{-b}^{+b} \frac{\log r\,.\,dy}{\sqrt{(b^2-y^2)}} = \int_0^\pi \log(\tfrac{1}{2}b)\,d\theta + \int_0^\alpha \log 2(\cos\theta - \cos\alpha)\,d\theta$$

$$+ \int_\alpha^\pi \log 2(\cos\alpha - \cos\theta)\,d\theta = \pi\log(\tfrac{1}{2}b)$$

$$+ \int_0^\pi \log\left\{2\sin\frac{\alpha+\theta}{2}\right\}d\theta + \int_0^\alpha \log\left\{2\sin\frac{\alpha-\theta}{2}\right\}d\theta + \int_\alpha^\pi \log\left\{2\sin\frac{\theta-\alpha}{2}\right\}d\theta$$

$$= \pi\log\tfrac{1}{2}b + 2\int_{\frac{1}{2}\alpha}^{\frac{1}{2}\pi+\frac{1}{2}\alpha} \log(2\sin\phi)\,d\phi + \int_0^{\frac{1}{2}\alpha} \log(2\sin\phi)\,d\phi + 2\int_0^{\frac{1}{2}\pi-\frac{1}{2}\alpha} \log(2\sin\phi)\,d\phi$$

$$= \pi\log\tfrac{1}{2}b + 2\int_0^{\frac{1}{2}\pi} \log(2\sin\phi)\,d\phi + 2\int_{\frac{1}{2}\pi}^{\frac{1}{2}\pi+\frac{1}{2}\alpha} \log(2\sin\phi)\,d\phi + 2\int_0^{\frac{1}{2}\pi-\frac{1}{2}\alpha} \log(2\sin\phi)\,d\phi$$

$$= \pi\log\tfrac{1}{2}b + 4\int_0^{\frac{1}{2}\pi} \log(2\sin\phi)\,d\phi,$$

as we see by changing ϕ into $\pi-\phi$ in the second integral. Since α has disappeared, the original integral is independent of η. In fact,*

$$\int_0^{\frac{1}{2}\pi} \log(2\sin\phi)\,d\phi = 0,$$

and we have

$$\int_{-b}^{+b} \frac{\log r\,.\,dy}{\sqrt{(b^2-y^2)}} = \pi\log\tfrac{1}{2}b, \tag{23}$$

as in the particular case of $\eta = 0$.

The required condition (17) can thus be satisfied by the proposed form of Ψ, provided that kb be small enough. When kb is greater, the resulting value of ψ in (15) will no longer be constant over the aperture, but we may find what the actual value is as a function of η by carrying out the integration with inclusion of more terms in the series representing D. As a preliminary, it will be convenient to discuss certain definite integrals which present themselves. The first of the series, which has already occurred, we will call h_0, so that

$$h_0 = \int_0^{\frac{1}{2}\pi} \log(2\sin\theta)\,d\theta = \int_0^{\frac{1}{2}\pi} \log(2\cos\theta)\,d\theta = \tfrac{1}{2}\int_0^{\frac{1}{2}\pi} \log(2\sin 2\theta)\,d\theta$$

$$= \tfrac{1}{4}\int_0^{\pi} \log(2\sin\phi)\,d\phi = \tfrac{1}{2}\int_0^{\frac{1}{2}\pi} \log(2\sin\phi)\,d\phi = \tfrac{1}{2}h_0$$

* See below.

Accordingly, $h_0 = 0$. More generally we set, n being any even integer,

$$h_n = \int_0^{\frac{1}{2}\pi} \sin^n\theta \log(2\sin\theta)\, d\theta, \qquad (24)$$

or, on integration by parts,

$$h_n = \int_0^{\frac{1}{2}\pi} \cos\theta \left\{(n-1)\sin^{n-2}\theta\cos\theta\log(2\sin\theta) + \sin^{n-2}\theta\cos\theta\right\} d\theta$$

$$= (n-1)(h_{n-2} - h_n) + \int_0^{\frac{1}{2}\pi} (\sin^{n-2}\theta - \sin^n\theta)\, d\theta.$$

Thus $$h_n = \frac{n-1}{n} h_{n-2} + \frac{1}{n^2}\,\frac{n-3,\ n-5 \ldots 1}{n-2,\ n-4 \ldots 2}\,\frac{\pi}{2}, \qquad (25)$$

by which the integrals h_n can be calculated in turn. Thus

$$h_2 = \pi/8,$$

$$h_4 = \frac{3}{4} h_2 + \frac{1}{4^2}\cdot\frac{1}{2}\cdot\frac{\pi}{2} = \frac{\pi}{2}\,\frac{3\,.\,1}{4\,.\,2}\left(\frac{1}{1\,.\,2} + \frac{1}{3\,.\,4}\right),$$

$$h_6 = \frac{5\,.\,3\,.\,1}{6\,.\,4\,.\,2}\,\frac{\pi}{2}\left(\frac{1}{1\,.\,2} + \frac{1}{3\,.\,4}\right) + \frac{1}{6^2}\,\frac{3\,.\,1}{4\,.\,2}\,\frac{\pi}{2}$$

$$= \frac{\pi}{2}\,\frac{5\,.\,3\,.\,1}{6\,.\,4\,.\,2}\left(\frac{1}{1\,.\,2} + \frac{1}{3\,.\,4} + \frac{1}{5\,.\,6}\right).$$

Similarly $$h_8 = \frac{\pi}{2}\,\frac{7\,.\,5\,.\,3\,.\,1}{8\,.\,6\,.\,4\,.\,2}\left(\frac{1}{1\,.\,2} + \frac{1}{3\,.\,4} + \frac{1}{5\,.\,6} + \frac{1}{7\,.\,8}\right),$$ and so on

It may be remarked that the series within brackets, being equal to

$$1 - \tfrac{1}{2} + \tfrac{1}{3} - \tfrac{1}{4} + \ldots,$$

approaches ultimately the limit log 2. A tabulation of the earlier members of the series of integrals will be convenient:—

Table I.

$2h_0/\pi = 0$

$2h_2/\pi = 1/4 = 0{\cdot}25$

$2h_4/\pi = 7/32 = 0{\cdot}21875$

$2h_6/\pi = 37/192 = 0{\cdot}19271$

$2h_8/\pi = 533/3072 = 0{\cdot}17350$

$2h_{10}/\pi = 1627/10240 = 0{\cdot}15889$

$2h_{12}/\pi = 18107/122880 = 0{\cdot}14736$

$2h_{14}/\pi =$ .... $= 0{\cdot}13798$

$2h_{16}/\pi =$ .... $= 0{\cdot}13018$

$2h_{18}/\pi =$ .... $= 0{\cdot}12356$

$2h_{20}/\pi =$ .... $= 0{\cdot}11784$

The last four have been calculated in sequence by means of (25).

In (24) we may, of course, replace $\sin\theta$ by $\cos\theta$ throughout. If both $\sin\theta$ and $\cos\theta$ occur, as in

$$\int_0^{\frac{1}{2}\pi} \sin^n\theta\cos^m\theta\log(2\sin\theta)\,d\theta, \tag{26}$$

where n and m are even, we may express $\cos^m\theta$ by means of $\sin\theta$, and so reduce (26) to integrals of the form (24). The particular case where $m = n$ is worthy of notice. Here

$$\int_0^{\frac{1}{2}\pi} \sin^n\theta\cos^n\theta\log(2\sin\theta)\,d\theta = \int_0^{\frac{1}{2}\pi} \sin^n\theta\cos^n\theta\log(2\cos\theta)\,d\theta$$

$$= \tfrac{1}{2}\int_0^{\frac{1}{2}\pi} \frac{\sin^n 2\theta}{2^n}\log(2\sin 2\theta)\,d\theta = \frac{h_n}{2^{n+1}}. \tag{27}$$

A comparison of the two treatments gives a relation between the integrals h. Thus, if $n=4$,

$$h_4 - 2h_6 + h_8 = h_4/2^5.$$

We now proceed to the calculation of the left-hand member of (17) with $\Psi = (b^2-y^2)^{-\frac{1}{2}}$, or, as it may be written,

$$\int_{-b}^{+b} \frac{dy}{\sqrt{(b^2-\eta^2)}}\left[\left(\gamma+\log\frac{ikr}{2}\right)J_0(kr)+\frac{k^2r^2}{2^2}-\frac{k^4r^4}{2^2.4^2}S_2+\frac{k^6r^6}{2^2.4^2.6^2}S_3-\ldots\right]. \tag{28}$$

The leading term has already been found to be

$$\pi\left(\gamma+\log\frac{ikb}{4}\right). \tag{29}$$

In (28) r is equal to $\pm(y-\eta)$. Taking, as before,

$$y = b\cos\theta, \qquad \eta = b\cos\alpha,$$

we have

$$\int_0^{\pi} d\theta\left[\left\{\gamma+\log\frac{ikb}{4}+\log\pm 2(\cos\theta-\cos\alpha)\right\}J_0\{kb(\cos\theta-\cos\alpha)\}\right.$$

$$\left.+\frac{k^2b^2(\cos\theta-\cos\alpha)^2}{2^2}-\frac{k^4b^4(\cos\theta-\cos\alpha)^4}{2^2.4^2}\cdot\frac{3}{2}+\frac{k^6b^6(\cos\theta-\cos\alpha)^6}{2^2.4^2.6^2}\cdot\frac{11}{6}-\ldots\right]. \tag{30}$$

As regards the terms which do not involve $\log(\cos\theta-\cos\alpha)$, we have to deal merely with

$$\int_0^{\pi}(\cos\theta-\cos\alpha)^n\,d\theta, \tag{31}$$

where n is an even integer, which, on expansion of the binomial and integration by a known formula, becomes

$$\pi\left[\frac{n-1.n-3.n-5\ldots1}{n.n-2.n-4\ldots2}+\frac{n.n-1}{1.2}\,\frac{n-3.n-5\ldots1}{n-2.n-4\ldots2}\cos^2\alpha\right.$$

$$\left.+\frac{n.n-1.n-2.n-3}{1.2.3.4}\,\frac{n-5.n-7\ldots1}{n-4.n-6\ldots2}\cos^4\alpha+\ldots+\cos^n\alpha\right]. \tag{32}$$

Thus, if $n = 2$, we get $\pi\left[\frac{1}{2}+\cos^2\alpha\right]$. If $n = 4$,

$$\pi\left[\frac{3\,.\,1}{4\,.\,2}+\frac{4\,.\,3}{1\,.\,2}\,\frac{1}{2}\cos^2\alpha+\cos^4\alpha\right], \quad \text{and so on.}$$

The coefficient of (31), or (32), in (30) is

$$(-1)^{\frac{1}{2}n}\,\frac{k^n b^n}{2^2\,.\,4^2\ldots n^2}\left[\gamma+\log\frac{ikb}{4}-S_{\frac{1}{2}n}\right]. \tag{33}$$

At the centre of the aperture where $\eta = 0$, $\cos\alpha = 0$, (32) reduces to its first term. At the edges where $\cos\alpha = \pm 1$, we may obtain a simpler form directly from (31). Thus

$$(31) = \int_0^\pi (1\pm\cos\theta)^n\,d\theta = 2^n\pi\,\frac{2n-1\,.\,2n-3\ldots 1}{2n\,.\,2n-2\ldots 2} = \pi\,\frac{2n-1\,.\,2n-3\ldots 1}{n\,.\,n-1\,.\,n-2\ldots 1}. \tag{34}$$

For example, if $n = 6$,

$$(34) = \pi\,\frac{11\,.\,9\,.\,7\,.\,5\,.\,3\,.\,1}{6\,.\,5\,.\,4\,.\,3\,.\,2\,.\,1} = \frac{231\,\pi}{16}.$$

We have also in (30) to consider (n even)

$$\begin{aligned}
&2^{-n}\int_0^\pi d\theta\,(\cos\theta-\cos\alpha)^n\log\{\pm 2(\cos\theta-\cos\alpha)\}\\
&= \int_0^\alpha d\theta\,\sin^n\frac{\theta+\alpha}{2}\,\sin^n\frac{\theta-\alpha}{2}\,\log\left\{4\sin\frac{\theta+\alpha}{2}\,\sin\frac{\alpha-\theta}{2}\right\}\\
&\quad+\int_\alpha^\pi d\theta\,\sin^n\frac{\theta+\alpha}{2}\,\sin^n\frac{\theta-\alpha}{2}\,\log\left\{4\sin\frac{\theta+\alpha}{2}\,\sin\frac{\theta-\alpha}{2}\right\}\\
&= \int_0^\pi d\theta\,\sin^n\frac{\theta+\alpha}{2}\,\sin^n\frac{\theta-\alpha}{2}\,\log\left\{2\sin\frac{\theta+\alpha}{2}\right\}\\
&\quad+\int_0^\alpha d\theta\,\sin^n\frac{\theta+\alpha}{2}\,\sin^n\frac{\theta-\alpha}{2}\,\log\left\{2\sin\frac{\alpha-\theta}{2}\right\}\\
&\quad+\int_\alpha^\pi d\theta\,\sin^n\frac{\theta+\alpha}{2}\,\sin^n\frac{\theta-\alpha}{2}\,\log\left\{2\sin\frac{\theta-\alpha}{2}\right\}\\
&= 2\int_0^{\frac{1}{2}\pi+\frac{1}{2}\alpha} d\phi\,\sin^n\phi\,\sin^n(\phi-\alpha)\,\log(2\sin\phi)\\
&\quad+2\int_0^{\frac{1}{2}\pi-\frac{1}{2}\alpha} d\phi\,\sin^n\phi\,\sin^n(\phi+\alpha)\,\log(2\sin\phi)\\
&= 2\int_0^{\frac{1}{2}\pi} d\phi\,\sin^n\phi\,\{\sin^n(\phi-\alpha)+\sin^n(\phi+\alpha)\}\,\log(2\sin\phi)\\
&\quad+2\int_{\frac{1}{2}\pi}^{\frac{1}{2}\pi+\frac{1}{2}\alpha} d\phi\,\sin^n\phi\,\sin^n(\phi-\alpha)\,\log(2\sin\phi)\\
&\quad-2\int_{\frac{1}{2}\pi-\frac{1}{2}\alpha}^{\frac{1}{2}\pi} d\phi\,\sin^n\phi\,\sin^n(\phi+\alpha)\,\log(2\sin\phi)\\
&= 2\int_0^{\frac{1}{2}\pi} d\phi\,\sin^n\phi\,\{\sin^n(\phi-\alpha)+\sin^n(\phi+\alpha)\}\,\log(2\sin\phi),
\end{aligned} \tag{35}$$

since the last two integrals cancel, as appears when we write $\pi-\psi$ for ϕ, n being even.

In (35)

$$\tfrac{1}{2}\sin^n(\phi+\alpha)+\tfrac{1}{2}\sin^n(\phi-\alpha) = \sin^n\phi\cos^n\alpha$$

$$+\frac{n\,.\,n-1}{1\,.\,2}\sin^{n-2}\phi\cos^2\phi\sin^2\alpha\cos^{n-2}\alpha$$

$$+\frac{n\,.\,n-1\,.\,n-2\,.\,n-3}{1\,.\,2\,.\,3\,.\,4}\sin^{n-4}\phi\cos^4\phi\sin^4\alpha\cos^{n-4}\alpha+\ldots+\cos^n\phi\sin^n\alpha, \tag{36}$$

and thus the result may be expressed by means of the integrals h. Thus if $n=2$,

$$(35) = 4\int_0^{\frac{1}{2}\pi}d\phi\sin^2\phi\left\{\sin^2\phi\cos^2\alpha+\cos^2\phi\sin^2\alpha\right\}\log(2\sin\phi)$$

$$= 4\left\{(\cos^2\alpha-\sin^2\alpha)\,h_4+\sin^2\alpha\,h_2\right\}. \tag{37}$$

If $n=4$,

$$(35) = 4\int_0^{\frac{1}{2}\pi}d\phi\sin^4\phi\left\{\sin^4\phi\cos^4\alpha+6\sin^2\phi\cos^2\phi\sin^2\alpha\cos^2\alpha\right.$$
$$\left.+\cos^4\phi\sin^4\alpha\right\}\log(2\sin\phi)$$

$$= 4\left\{(\cos^4\alpha-6\sin^2\alpha\cos^2\alpha+\sin^4\alpha)\,h_8\right.$$
$$\left.+(6\sin^2\alpha\cos^2\alpha-2\sin^4\alpha)\,h_6+\sin^4\alpha\,h_4\right\}. \tag{38}$$

If $n=6$,

$$(35) = 4\left\{(\cos^6\alpha-15\cos^4\alpha\sin^2\alpha+15\cos^2\alpha\sin^4\alpha-\sin^6\alpha)\,h_{12}\right.$$
$$+(15\cos^4\alpha\sin^2\alpha-30\cos^2\alpha\sin^4\alpha+3\sin^6\alpha)\,h_{10}$$
$$\left.+(15\cos^2\alpha\sin^4\alpha-3\sin^6\alpha)\,h_8+\sin^6\alpha\,h_6\right\}. \tag{39}$$

It is worthy of remark that if we neglect the small differences between the h's in (39), it reduces to $4\cos^6\alpha\,h_{12}$, and similarly in other cases.

When n is much higher than 6, the general expressions corresponding to (37), (38), (39) become complicated. If, however, $\cos\alpha$ be either 0, or ± 1, (36) reduces to a single term, viz., $\cos^n\phi$ or $\sin^n\phi$. Thus at the centre ($\cos\alpha=0$) from either of its forms

$$(35) = 2^{-n}\,.\,2h_n. \tag{40}$$

On the other hand, at the edges ($\cos\alpha=\pm 1$)

$$(35) = 4\int_0^{\frac{1}{2}\pi}d\phi\sin^{2n}\phi\log(2\sin\phi) = 4h_{2n}. \tag{41}$$

In (30), the object of our quest, the integral (35) occurs with the coefficient

$$(-1)^{\frac{1}{2}n}\frac{2^n k^n b^n}{2^2\,.\,4^2\,.\,6^2\ldots n^2}. \tag{42}$$

Thus, expanded in powers of kb, (28) or (30) becomes

$$\pi\left(\gamma+\log\frac{ikb}{4}\right)-\frac{\pi k^2b^2}{2^2}\left[\left\{\gamma+\log\frac{ikb}{4}-1\right\}\left\{\tfrac{1}{2}+\cos^2\alpha\right\}\right.$$
$$\left.+\frac{2^3.2h_4}{\pi}(\cos^2\alpha-\sin^2\alpha)+\frac{2^3.2h_2}{\pi}\sin^2\alpha\right]$$
$$+\frac{\pi k^4b^4}{2^2.4^2}\left[\left\{\gamma+\log\frac{ikb}{4}-\frac{3}{2}\right\}\left\{\frac{3}{8}+3\cos^2\alpha+\cos^4\alpha\right\}\right.$$
$$+\frac{2^5.2h_8}{\pi}(\cos^4\alpha-6\cos^2\alpha\sin^2\alpha+\sin^4\alpha)$$
$$\left.+\frac{2^5.2h_6}{\pi}(6\cos^2\alpha\sin^2\alpha-2\sin^4\alpha)+\frac{2^5.2h_4}{\pi}\sin^4\alpha\right]$$
$$-\frac{\pi k^6b^6}{2^2.4^2.6^2}\left[\left\{\gamma+\log\frac{ikb}{4}-\frac{11}{6}\right\}\left\{\frac{5}{16}+\frac{45}{8}\cos^2\alpha+\frac{15}{2}\cos^4\alpha+\cos^6\alpha\right\}\right.$$
$$+\frac{2^7.2h_{12}}{\pi}(\cos^6\alpha-15\cos^4\alpha\sin^2\alpha+15\cos^2\alpha\sin^4\alpha-\sin^6\alpha)$$
$$+\frac{2^7.2h_{10}}{\pi}(15\cos^4\alpha\sin^2\alpha-30\cos^2\alpha\sin^4\alpha+3\sin^6\alpha)$$
$$\left.+\frac{2^7.2h_8}{\pi}(15\cos^2\alpha\sin^4\alpha-3\sin^6\alpha)+\frac{2^7.2h_6}{\pi}\sin^6\alpha\right]+\ldots\ldots \qquad (43)$$

At the centre of the aperture ($\cos\alpha=0$), in virtue of (40), a simpler form is available. We have

$$\pi\left(\gamma+\log\frac{ikb}{4}\right)-\frac{\pi k^2b^2}{2^2}\left[\frac{1}{2}\left(\gamma+\log\frac{ikb}{4}-1\right)+\frac{2h_2}{\pi}\right]$$
$$+\frac{\pi k^4b^4}{2^2.4^2}\left[\frac{3.1}{4.2}\left(\gamma+\log\frac{ikb}{4}-\frac{3}{2}\right)+\frac{2h_4}{\pi}\right]$$
$$-\frac{\pi k^6b^6}{2^2.4^2.6^2}\left[\frac{5.3.1}{6.4.2}\left(\gamma+\log\frac{ikb}{4}-\frac{11}{6}\right)+\frac{2h_6}{\pi}\right]$$
$$+\frac{\pi k^8b^8}{2^2.4^2.6^2.8^2}\left[\frac{7.5.3.1}{8.6.4.2}\left(\gamma+\log\frac{ikb}{4}-\frac{25}{12}\right)+\frac{2h_8}{\pi}\right]-\ldots. \qquad (44)$$

Similarly at the edges, by (34), (41), we have

$$\pi\left(\gamma+\log\frac{ikb}{4}\right)-\frac{\pi k^2b^2}{2^2}\left[\frac{3.1}{2.1}\left(\gamma+\log\frac{ikb}{4}-1\right)+2^3\frac{2h_4}{\pi}\right]$$
$$+\frac{\pi k^4b^4}{2^2.4^2}\left[\frac{7.5.3.1}{4.3.2.1}\left(\gamma+\log\frac{ikb}{4}-\frac{3}{2}\right)+2^5\frac{2h_8}{\pi}\right]$$
$$-\frac{\pi k^6b^6}{2^2.4^2.6^2}\left[\frac{11.9.7.5.3.1}{6.5.4.3.2.1}\left(\gamma+\log\frac{ikb}{4}-\frac{11}{6}\right)+2^7\frac{2h_{12}}{\pi}\right]+\ldots. \qquad (45)$$

For the general value of α, (43) is perhaps best expressed in terms of $\cos\alpha$, equal to η/b. With introduction of the values of h, we have

$$\begin{aligned}
&\pi\left(\gamma+\log\frac{ikb}{4}\right)-\frac{\pi k^2b^2}{2^2}\left[\left(\gamma+\log\frac{ikb}{4}\right)\left(\cos^2\alpha+\frac{1}{2}\right)+\frac{1}{2}\cos^2\alpha-\frac{1}{4}\right]\\
&+\frac{\pi k^4b^4}{2^2.4^2}\left[\left(\gamma+\log\frac{ikb}{4}\right)\left(\cos^4\alpha+3\cos^2\alpha+\frac{3}{8}\right)+\frac{7}{12}\cos^4\alpha-\frac{5}{4}\cos^2\alpha-\frac{11}{32}\right]\\
&-\frac{\pi k^6b^6}{2^2.4^2.6^2}\left[\left(\gamma+\log\frac{ikb}{4}\right)\left(\cos^6\alpha+\frac{15}{2}\cos^4\alpha+\frac{45}{8}\cos^2\alpha+\frac{5}{16}\right)\right.\\
&\left.+\frac{37}{60}\cos^6\alpha-\frac{23}{8}\cos^4\alpha-\frac{159}{32}\cos^2\alpha-\frac{73}{192}\right]+\dots\,.
\end{aligned}\tag{46}$$

These expressions are the values of

$$\int_{-b}^{+b}\frac{\mathrm{D}(kr)\,dy}{\sqrt{(b^2-y^2)}}\tag{47}$$

for the various values of η.

We now suppose that $kb=1$. The values for other particular cases, such as $kb=\frac{1}{2}$, may then easily be deduced. For $\cos\alpha=0$, from (44) we have

$$\begin{aligned}
&\pi\left(\gamma+\log\frac{i}{4}\right)\left[1-\frac{1}{2^2}\frac{1}{2}+\frac{1}{2^2.4^2}\frac{3.1}{4.2}-\frac{1}{2^2.4^2.6^2}\frac{5.3.1}{6.4.2}+\dots\right]\\
&\quad+\pi\left[\frac{1}{2^2}\frac{1}{4}-\frac{1}{2^2.4^2}\frac{11}{32}+\frac{1}{2^2.4^2.6^2}\frac{73}{192}-\dots\right]\\
&\qquad=\pi\left(\gamma+\log\frac{i}{4}\right)[1-0{\cdot}12500+0{\cdot}00586+0{\cdot}00013]\\
&\qquad\quad+\pi[0{\cdot}06250-0{\cdot}00537+0{\cdot}00016]\\
&\qquad=\pi\left(\gamma+\log\frac{i}{4}\right)\times0{\cdot}88073+\pi\times0{\cdot}05729\\
&\qquad=\pi[-0{\cdot}65528+1{\cdot}3834\,i],
\end{aligned}\tag{48}$$

since $\gamma=0{\cdot}577215$, $\log 2=0{\cdot}693147$, $\log i=\frac{1}{2}\pi i$.

In like manner, if $kb=\frac{1}{2}$, we get still with $\cos\alpha=0$,

$$\begin{aligned}
&\pi\left(\gamma+\log\frac{i}{8}\right)[1-0{\cdot}03125+0{\cdot}00037]+\pi[0{\cdot}01562-0{\cdot}00033]\\
&\qquad=\pi[-1{\cdot}4405+1{\cdot}5223\,i].
\end{aligned}\tag{49}$$

If $kb=2$, we have

$$\begin{aligned}
&\pi\left(\gamma+\log\frac{i}{2}\right)[1-0{\cdot}5+0{\cdot}0938-0{\cdot}0087+0{\cdot}0005]\\
&\qquad+\pi[0{\cdot}25-0{\cdot}0859+0{\cdot}0102-0{\cdot}0006]\\
&\quad=\pi[+0{\cdot}1058+0{\cdot}9199\,i].
\end{aligned}\tag{50}$$

If $kb = 1$ and $\cos\alpha = \pm 1$, we have from (45)

$$\pi\left(\gamma+\log\frac{i}{4}\right)\left[1-\frac{1}{2^2}\frac{3}{2}+\frac{1}{2^2.4^2}\frac{35}{8}-\frac{1}{2^2.4^2.6^2}\frac{231}{16}\right.$$

$$\left.+\frac{1}{2^2.4^2.6^2.8^2}\frac{6435}{128}-\frac{1}{2^2.4^2.6^2.8^2.10^2}\frac{19.17.6435}{10.9.128}+\ldots\right]$$

$$-\pi\left[\frac{1}{2^2}\frac{1}{4}+\frac{1}{2^2.4^2}\frac{97}{96}-\frac{1}{2^2.4^2.6^2}\frac{7303}{960}+\frac{38{\cdot}084}{2^2.4^2.6^2.8^2}-\frac{170{\cdot}64}{2^2.4^2.6^2.8^2.10^2}+\ldots\right]$$

$$=\pi\left(\gamma+\log\frac{i}{4}\right)[1-0{\cdot}375+0{\cdot}068359-0{\cdot}006266+0{\cdot}000341-0{\cdot}000012]$$

$$-\pi[0{\cdot}0625+0{\cdot}015788-0{\cdot}003302+0{\cdot}000258+0{\cdot}000012]$$

$$=\pi[-0{\cdot}63141+1{\cdot}0798\,i]. \tag{51}$$

Similarly, if $kb = \frac{1}{2}$, we have

$$\pi\left(\gamma+\log\frac{i}{8}\right)[1-0{\cdot}09375+0{\cdot}00427-0{\cdot}00010]$$

$$-\pi[0{\cdot}01562+0{\cdot}00099-0{\cdot}00005]$$

$$=\pi[-1{\cdot}3842+1{\cdot}4301\,i]. \tag{52}$$

And if $kb = 2$, with diminished accuracy,

$$\pi\left(\gamma+\log\frac{i}{2}\right)[1-1{\cdot}5+1{\cdot}094-0{\cdot}401+0{\cdot}087-0{\cdot}012+0{\cdot}001]$$

$$-\pi[0{\cdot}25+0{\cdot}253-0{\cdot}211+0{\cdot}066-0{\cdot}012+0{\cdot}001]$$

$$=\pi[-0{\cdot}378+0{\cdot}422\,i]. \tag{53}$$

As an intermediate value of α we will select $\cos^2\alpha = \frac{1}{2}$. For $kb = 1$ from (46)

$$\pi\left(\gamma+\log\frac{i}{4}\right)[1-0{\cdot}25+0{\cdot}03320-0{\cdot}00222+\ldots]$$

$$+\pi[0-0{\cdot}01286+0{\cdot}001522+\ldots]$$

$$=\pi[-0{\cdot}6432+1{\cdot}2268\,i]. \tag{54}$$

Also, when $kb = \frac{1}{2}$,

$$\pi[-1{\cdot}4123+1{\cdot}4759\,i]. \tag{55}$$

When $kb = 2$, only a rough value is afforded by (46), viz.,

$$\pi[-0{\cdot}16+0{\cdot}61\,i]. \tag{56}$$

The accompanying table exhibits the various numerical results, the factor π being omitted.

Table II.

	$kb = \frac{1}{2}$.	$kb = 1$.	$kb = 2$.
$\cos\alpha = 0$	$-1{\cdot}4405+1{\cdot}5223\,i$	$-0{\cdot}65528+1{\cdot}3834\,i$	$+0{\cdot}1058+0{\cdot}9199\,i$
$\cos^2\alpha = \frac{1}{2}$	$-1{\cdot}4123+1{\cdot}4759\,i$	$-0{\cdot}6432\ \ +1{\cdot}2268\,i$	$-0{\cdot}16\ \ +0{\cdot}61\,i$
$\cos^2\alpha = 1$	$-1{\cdot}3842+1{\cdot}4301\,i$	$-0{\cdot}63141+1{\cdot}0798\,i$	$-0{\cdot}378\ \ +0{\cdot}422\,i$

As we have seen already the tabulated quantity when kb is very small takes the form $\gamma + \log ikb/4$, or $\log kb - 0{\cdot}8091 + 1{\cdot}5708i$, whatever may be the value of α. In this case the condition (17) can be completely satisfied with $\Psi = \mathrm{A}(b^2 - y^2)^{-\frac{1}{2}}$, A being chosen suitably. When kb is finite, (17) can no longer be satisfied for all values of α. But when $kb = \frac{1}{2}$, or even when $kb = 1$, the tabulated number does not vary greatly with α and we may consider (17) to be approximately satisfied if we make in the first case

$$\pi(-1{\cdot}4123 + 1{\cdot}4759\,i)\,\mathrm{A} = -1, \tag{57}$$

and in the second,

$$\pi(-0{\cdot}6432 + 1{\cdot}2268\,i)\,\mathrm{A} = -1. \tag{58}$$

The value of ψ, applicable to a point at a distance directly in front of the aperture is then, as in (16),

$$\psi = -\pi\mathrm{A}\left(\frac{\pi}{2ikr}\right)^{\frac{1}{2}} e^{-ikr}. \tag{59}$$

In order to obtain a better approximation we require the aid of a second solution with a different form of Ψ. When this is introduced, as an addition to the first solution and again with an arbitrary constant multiplier, it will enable us to satisfy (17) for two distinct values of α, that is of η, and thus with tolerable accuracy over the whole range from $\cos\alpha = 0$ to $\cos\alpha = \pm 1$. Theoretically, of course, the process could be carried further so as to satisfy (17) for any number of assigned values of $\cos\alpha$.

As the second solution we will take simply $\Psi = 1$, so that the left-hand member of (17) is

$$\int_0^{b+\eta} \mathrm{D}(kr)\,dr + \int_0^{b-\eta} \mathrm{D}(kr)\,dr. \tag{60}$$

If we omit k, which may always be restored by consideration of homogeneity, we have

$$\begin{aligned}(60) = \left(\gamma + \log\frac{i}{2}\right)&\left[b + \eta - \frac{(b+\eta)^3}{2^2 . 3} + \frac{(b+\eta)^5}{2^2 . 4^2 . 5} - \dots\right] \\ &+ \frac{(b+\eta)^3}{2^2 . 3} - \frac{(b+\eta)^5}{2^2 . 4^2 . 5}\,\mathrm{S}_2 + \frac{(b+\eta)^7}{2^2 . 4^2 . 6^2 . 7}\,\mathrm{S}_3 - \dots \\ &+ (b+\eta)\{\log(b+\eta) - 1\} - \frac{(b+\eta)^3}{2^2 . 3}\left\{\log(b+\eta) - \frac{1}{3}\right\} \\ &+ \frac{(b+\eta)^5}{2^2 . 4^2 . 5}\left\{\log(b+\eta) - \frac{1}{5}\right\} - \dots\end{aligned}$$

+ the same expression with the sign of η changed.

The leading term in (60) is thus

$$2b(\gamma - 1 + \log\tfrac{1}{2}i) + (b+\eta)\log(b+\eta) + (b-\eta)\log(b-\eta). \tag{61}$$

At the centre of the aperture ($\eta = 0$)

$$(61) = 2b\{\gamma-1+\log \tfrac{1}{2} ib\},$$

and at the edges ($\eta = \pm b$),

$$(61) = 2b\{\gamma-1+\log ib\}.$$

It may be remarked that in (61), the real part varies with η, although the imaginary part is independent of that variable.

The complete expression (60) naturally assumes specially simple forms at the centre and edges of the aperture. Thus, when $\eta = 0$,

$$(60)\div 2b = \left(\gamma+\log\frac{ib}{2}\right)\Big[1-\frac{b^2}{2^2.3}+\frac{b^4}{2^2.4^2.5}-\ldots\Big|$$
$$-1+\frac{b^2}{2^2.3}\left(1+\frac{1}{3}\right)-\frac{b^4}{2^2.4^2.5}\left(1+\frac{1}{2}+\frac{1}{5}\right)+\frac{b^6}{2^2.4^2.6^2.7}\left(1+\frac{1}{2}+\frac{1}{3}+\frac{1}{7}\right)-\ldots; \tag{62}$$

and, similarly, when $\eta = \pm b$,

$$(60)\div 2b = (\gamma+\log ib)\Big[1-\frac{(2b)^2}{2^2.3}+\frac{(2b)^4}{2^2.4^2.5}-\ldots\Big|$$
$$-1+\frac{(2b)^2}{2^2.3}\left(1+\frac{1}{3}\right)-\frac{(2b)^4}{2^2.4^2.5}\left(1+\frac{1}{2}+\frac{1}{5}\right)+\frac{(2b)^6}{2^2.4^2.6^4.7}\left(1+\frac{1}{2}+\frac{1}{3}+\frac{1}{7}\right)-\ldots \tag{63}$$

To restore k we have merely to write kb for b in the *right-hand members* of (62), (63).

The calculation is straightforward. For the same values as before of kb and of $\cos^2\alpha$, equal to η^2/b^2, we get for $(60)\div 2b$

Table III.

η^2/b^2.	$kb = \frac{1}{2}$.	$kb = 1$.	$kb = 2$.
0	$-1\cdot7649+1\cdot5384\,i$	$-1\cdot0007+1\cdot4447\,i$	$-0\cdot2167+1\cdot1198\,i$
$\frac{1}{2}$	$-1\cdot4510+1\cdot4912\,i$	$-0\cdot6740+1\cdot2771\,i$	$-0\cdot1079+0\cdot7166\,i$
1	$-1\cdot0007+1\cdot4447\,i$	$-0\cdot2217+1\cdot1198\,i$	$+0\cdot1894+0\cdot4024\,i$

We now proceed to combine the two solutions, so as to secure a better satisfaction of (17) over the width of the aperture. For this purpose we determine A and B in

$$\Psi = \mathrm{A}\,(b^2-y^2)^{-\frac{1}{2}}+\mathrm{B}, \tag{64}$$

so that (17) may be exactly satisfied at the centre and edges ($\eta = 0$, $\eta = \pm b$). The departure from (17) when $\eta^2/b^2 = \frac{1}{2}$ can then be found. If for any value of kb and $\eta = 0$ the first tabular (complex) number is p and the second q, and for $\eta = \pm b$ the first is r and the second s, the equations of condition from (17) are

$$\pi\mathrm{A}.p+2b\mathrm{B}.q = -1, \qquad \pi\mathrm{A}.r+2b\mathrm{B}.s = -1. \tag{65}$$

When A and B are found, we have in (16)

$$\int_{-b}^{+b} \Psi \, dy = \pi \mathrm{A} + 2b\mathrm{B}.$$

From (65) we get

$$\pi \mathrm{A} = \frac{q-s}{ps-qr}, \qquad 2b\mathrm{B} = \frac{r-p}{ps-qr}, \tag{66}$$

so that

$$\int_{-b}^{+b} \Psi \, dy = \frac{q+r-s-p}{ps-qr}. \tag{67}$$

Thus for $kb = 1$ we have

$$p = -0{\cdot}65528 + 1{\cdot}38834\,i, \qquad q = -1{\cdot}0007 + 1{\cdot}4447\,i,$$

$$r = -0{\cdot}63141 + 1{\cdot}0798\,i, \qquad s = -0{\cdot}2217 + 1{\cdot}1198\,i,$$

whence

$$\pi \mathrm{A} = +0{\cdot}60008 + 0{\cdot}51828\,i, \qquad 2b\mathrm{B} = -0{\cdot}2652 + 0{\cdot}1073\,i,$$

and

$$(67) = +0{\cdot}3349 + 0{\cdot}6256\,i.$$

The above values of πA and $2b$B are derived according to (17) from the values at the centre and edges of the aperture. The success of the method may be judged by substitution of the values for $\eta^2/b^2 = \frac{1}{2}$. Using these in (17) we get $-0{\cdot}9801 - 0{\cdot}0082\,i$, for what should be -1, a very fair approximation.

In like manner, for $kb = 2$

$$(67) = +0{\cdot}259 + 1{\cdot}2415\,i.$$

and for $kb = \frac{1}{2}$

$$(67) = +0{\cdot}3378 + 0{\cdot}3526\,i.$$

As appears from (16), when k is given, the modulus of (67) may be taken to represent the amplitude of disturbance at a distant point immediately in front, and it is this with which we are mainly concerned. The following table gives the values of Mod. and Mod.² for several values of kb. The first three have been calculated from the simple formula, see (20).

Table IV.

kb.	Mod.².	Mod
0·01	0·0174	0·1320
0·05	0·0590	0·2429
0·25	0·1372	0·3704
0·50	0·2384	0·4883
1·00	0·5035	0·7096
2·00	1·608	1·268

The results are applicable to the problem of aerial waves, or shallow water waves, transmitted through a slit in a thin fixed wall, and to electric (luminous) waves transmitted by a similar slit in a thin perfectly opaque screen, provided that the electric vector is *perpendicular* to the length of the slit.

In curve A, fig. 1, the value of the modulus from the third column of Table IV is plotted against kb.

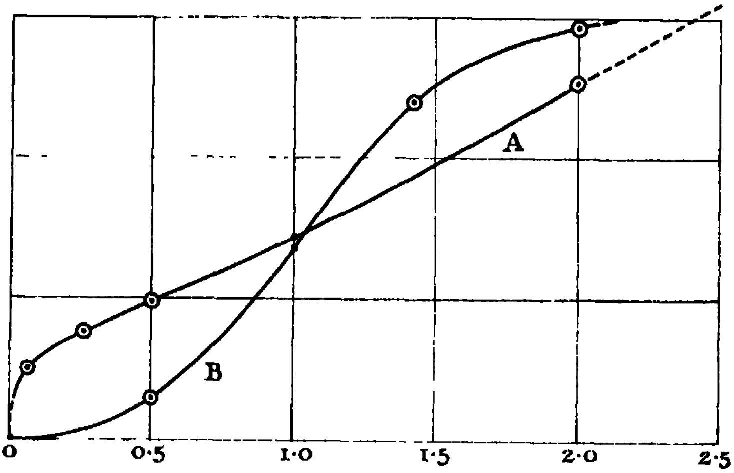

Fig. 1.

When kb is large, the limiting form of (67) may be deduced from a formula, analogous to (12), connecting Ψ and $d\phi/dn$. As in (11),

$$\frac{d\psi}{dx} = \int \Psi \frac{dD}{dx}\,dy,$$

in which, when x is very small, we may take $D = \log r$. Thus

$$\frac{d\psi}{dx} = \Psi \int_{-\infty}^{+\infty} \frac{x\,dy}{x^2+y^2} = \Psi \left[\tan^{-1}\frac{y}{x}\right]_{-\infty}^{+\infty} = \pi\Psi, \qquad \text{or} \qquad \Psi = \frac{1}{\pi}\frac{dx}{dn}. \quad (68)$$

Now, when kb is large, $d\psi/dn$ tends, except close to the edges, to assume the value ik, and ultimately

$$(67) = \int_{-b}^{+b} \Psi\,dy = \frac{2\,ikb}{\pi}, \quad (69)$$

of which the modulus is $2kb/\pi$ simply, *i.e.* $0{\cdot}637kb$.

We now pass on to consider case (ii), where the boundary condition to be satisfied over the wall is $\phi = 0$. Separating from ϕ the solution (χ) which would obtain were the wall unperforated, we have

$$\chi_m = e^{-ikx} - e^{ikx}, \qquad \chi_p = 0, \quad (70)$$

giving over the whole plane ($x = 0$),

$$\chi_m = 0, \qquad \chi_p = 0, \qquad d\chi_m/dx = -2ik, \qquad d\chi_p/dx = 0.$$

The supplementary solutions ψ, equal to $\phi-\chi$, may be written

$$\psi_m = \int \frac{dD}{dx} \Psi_m dy, \qquad \psi_p = \int \frac{dD}{dx} \Psi_p dy, \tag{71}$$

where Ψ_m, Ψ_p are functions of y, and the integrations are over the aperture. D as a function of r is given by (13), and r, denoting the distance between dy and the point (x, η), at which ψ_m, ψ_p are estimated, is equal to $\sqrt{\{x^2+(y-\eta)^2\}}$. The form (71) secures that on the *walls* $\psi_m = \psi_p = 0$, so that the condition of evanescence there, already satisfied by χ, is not disturbed. It remains to satisfy over the *aperture*.

$$\psi_m = \psi_p, \qquad -2ik + d\psi_m/dx = d\psi_p/dx. \tag{72}$$

The first of these is satisfied if $\Psi_m = -\Psi_p$, so that ψ_m and ψ_p are equal at any pair of corresponding points on the two sides. The values of $d\psi_m/dx$, $d\psi_p/dx$ are then opposite, and the remaining condition is also satisfied if

$$d\psi_m/dx = ik, \qquad d\psi_p/dx = -ik. \tag{73}$$

At a distance, and if the slit is very narrow, dD/dx may be removed from under the integral sign, so that

$$\psi_p = \frac{dD}{dx} \int_{-b}^{+b} \Psi_p dy, \tag{74}$$

in which

$$\frac{dD}{dx} = \frac{ikx}{r} \left(\frac{\pi}{2ikr} \right)^{\frac{1}{2}} e^{-ikr}. \tag{75}$$

And, even if kb be not small, (74) remains applicable if the distant point be directly in front of the slit, so that $x = r$. For such a point

$$\psi_p = ik \left(\frac{\pi}{2ikr} \right)^{\frac{1}{2}} e^{-ikr} \int_{-b}^{+b} \Psi_p dy. \tag{76}$$

There is a simple relation, analogous to (68), between the value of Ψ_p at any point (η) of the aperture and that of ψ_p at the same point. For in the application of (71) only those elements of the integral contribute which lie infinitely near the point where ψ_p is to be estimated, and for these $dD/dx = x/r^2$. The evaluation is effected by considering in the first instance a point for which x is finite and afterwards passing to the limit. Thus

$$\psi_p = \Psi_p \int \frac{x\,dy}{x^2+(y-\eta)^2} = \pi\Psi_p. \tag{77}$$

It remains to find, if possible, a form for Ψ_p, or ψ_p, which shall make $d\psi_p/dx$ constant over the aperture, as required by (73). In my former paper, dealing with the case where kb is very small, it was shown that known theorems relating to the flow of incompressible fluids lead to the desired conclusion. It appeared that (74), (75) give

$$\psi_p = -\frac{k^2 b^2 x}{2r}\left(\frac{\pi}{2ikr}\right)^{\frac{1}{2}} e^{-ikr}, \tag{78}$$

showing that when b is small the transmission falls off greatly, much more than in case (i), see (20). The realised solution from (78) is

$$\psi_p = -\frac{k^2 b^2 x}{2r}\left(\frac{\pi}{2kr}\right)^{\frac{1}{2}} \cos\left(nt - kr - \tfrac{1}{4}\pi\right), \tag{79}$$

corresponding to $\chi_m = 2 \sin nt \sin kx.$ (80)

The former method arrived at a result by assuming certain hydrodynamical theorems. For the present purpose we have to go further, and it will be appropriate actually to verify the constancy of $d\psi/dx$ over the aperture as resulting from the assumed form of Ψ, when kb is small. In this case we may take $D = \log r$, where $r^2 = x^2 + (y-\eta)^2$. From (71), the suffix p being omitted,

$$\frac{d\psi}{dx} = \int_{-b}^{+b} \frac{d^2 D}{dx^2} \Psi \, dy;$$

and herein $\dfrac{d^2 D}{dx^2} = -\dfrac{d^2 D}{d\eta^2} = -\dfrac{d^2 D}{dy^2}$ (η const.).

Thus, on integration by parts,

$$\frac{d\psi}{dx} = -\left[\Psi \frac{dD}{dy}\right] + \int_{-b}^{+b} \frac{dD}{dy}\frac{d\Psi}{dy}\, dy. \tag{81}$$

In (81) $\dfrac{dD}{dy} = \dfrac{dD}{dr}\dfrac{dr}{dy} = \dfrac{y-\eta}{(y-\eta)^2 + x^2},$

and so long as η is not equal to $\pm b$, it does not become infinite at the limits ($y = \pm b$), even though $x = 0$. Thus, if Ψ vanish at the limits, the integrated terms in (81) disappear. We now assume for trial

$$\Psi = \sqrt{(b^2 - y^2)}, \tag{82}$$

which satisfies the last-mentioned condition. Writing

$$y = b\cos\theta, \qquad \eta = b\cos\alpha, \qquad x' = x/b,$$

we have

$$-\frac{d\psi}{dx} = \int_0^\pi \frac{(\cos\theta - \cos\alpha)^2 + \cos\alpha\,(\cos\theta - \cos\alpha)}{(\cos\theta - \cos\alpha)^2 + x'^2}\, d\theta. \tag{83}$$

Of the two parts of the integral on the right in (83) the first yields π when $x' = 0$. For the second we have to consider

$$\int_0^\pi \frac{\cos\theta - \cos\alpha}{(\cos\theta - \cos\alpha)^2 + x'^2}\, d\theta, \tag{84}$$

in which $\cos\theta - \cos\alpha$ passes through zero within the range of integration. It will be shown that (84) vanishes ultimately when $x' = 0$. To this end the range of integration is divided into three parts: from 0 to α_1, where $\alpha_1 < \alpha$, from α_1 to α_2 where $\alpha_2 > \alpha$, and lastly from α_2 to π. In evaluating the first and third parts we may put $x' = 0$ at once. And if $z = \tan\frac{1}{2}\theta$

$$\int \frac{d\theta}{\cos\theta - \cos\alpha} = \frac{1}{\sin\alpha}\int\left\{\frac{dz}{\tan\frac{1}{2}\alpha + z} + \frac{dz}{\tan\frac{1}{2}\alpha - z}\right\}.$$

Sin α being omitted, the first and third parts together are thus

$$\log\frac{z+t}{z-t} + \log\frac{t+t_1}{t-t_1} + \log\frac{t_2-t}{t_2+t},$$

where $t = \tan\frac{1}{2}\alpha$, $t_1 = \tan\frac{1}{2}\alpha_1$, $t_2 = \tan\frac{1}{2}\alpha_2$, and z is to be made infinite.

It appears that the two parts taken together vanish, provided t_1, t_2 are so chosen that $t^2 = t_1t_2$.

It remains to consider the second part, viz.,

$$\int_{\alpha_1}^{\alpha_2} \frac{d\theta\,(\cos\theta - \cos\alpha)}{(\cos\theta - \cos\alpha)^2 + x'^2}, \tag{85}$$

in which we may suppose the range of integration $\alpha_2 - \alpha_1$ to be very small. Thus

$$(85) = \int_{\alpha_1}^{\alpha_2} \frac{d\theta\,.\,2\sin\frac{1}{2}(\theta+\alpha)\,\sin\frac{1}{2}(\alpha-\theta)}{4\sin^2\frac{1}{2}(\theta+\alpha)\,\sin^2\frac{1}{2}(\alpha-\theta) + x'^2}$$

$$= -\frac{1}{2\sin\alpha}\log\frac{\sin^2\alpha\,(\alpha_2-\alpha)^2 + x'^2}{\sin^2\alpha\,(\alpha-\alpha_1)^2 + x'^2},$$

and this also vanishes if $\alpha_2 - \alpha = \alpha - \alpha_1$, a condition consistent with the former to the required approximation. We infer that in (83)

$$-\frac{d\Psi}{dx} = \pi, \tag{86}$$

so that, with the aid of a suitable multiplier, (73) can be satisfied. Thus if $\Psi = A\sqrt{(b^2 - y^2)}$, (73) gives $A = ik/\pi$, and the introduction of this into (74) gives (78). We have now to find what departure from (86) is entailed when kb is no longer very small.

Since, in general,

$$d^2D/dx^2 + d^2D/dy^2 + k^2D = 0,$$

we find, as in (81),

$$-\frac{d\Psi}{dx} = k^2\int \Psi D\,dy - \int\frac{d\Psi}{dy}\frac{dD}{dy}\,dy, \tag{87}$$

and for the present Ψ has the value defined in (82). The first term on the right of (87) may be treated in the same way as (28) of the former problem, the difference being that $\sqrt{(b^2 - y^2)}$ occurs now in the numerator instead of the denominator. In (30) we are to introduce under the integral sign the additional factor $k^2b^2\sin^2\theta$. As regards the second term of (87) we have

$$-\int\frac{d\Psi}{dy}\frac{dD}{dy}\,dy = \int_{-b}^{+b}\frac{y\,(y-\eta)\,dy}{\sqrt{(b^2-y^2)}}\,\frac{1}{r}\,\frac{dD}{dr},$$

where in $\frac{1}{r}\frac{dD}{dr}$ we are to replace r by $\pm(y-\eta)$. We then assume as before $= b\cos\theta$, $\eta = b\cos\alpha$, and the same definite integrals h_n suffice; but the calculations are more complicated.

We have seen already that the leading term in (87) is π. For the next term we have

$$D = \gamma+\log\frac{ikr}{2}, \qquad \frac{1}{r}\frac{dD}{dr} = \frac{k^2}{4}-\frac{k^2}{2}\left(\gamma+\log\frac{ikr}{2}\right),$$

and thus

$$-\frac{1}{k^2b^2}\frac{d\psi}{dx} = \frac{\pi}{4}\left(\gamma+\log\frac{ikb}{4}+\frac{1}{2}\right)$$
$$+\int_0^\pi d\theta\,(1-\tfrac{3}{2}\cos^2\theta+\tfrac{1}{2}\cos\alpha\cos\theta)\log\pm 2\,(\cos\theta-\cos\alpha). \qquad (88)$$

The latter integral may be transformed into

$$2\int_0^{\frac{1}{2}\pi}d\phi\,\{1-\tfrac{3}{2}\cos^2(2\phi-\alpha)+\tfrac{1}{2}\cos\alpha\cos(2\phi-\alpha)$$
$$+1-\tfrac{3}{2}\cos^2(2\phi+\alpha)+\tfrac{1}{2}\cos\alpha\,(\cos 2\phi+\alpha)\}\log(2\sin\phi),$$

and this by means of the definite integrals h is found to be

$$-\frac{\pi}{8}(1+2\sin^2\alpha).$$

To this order of approximation the complete value is

$$-\frac{d\psi}{dx} = \pi+\tfrac{1}{4}\pi k^2b^2\,(\gamma-\sin^2\alpha+\log\tfrac{1}{4}ikb). \qquad (89)$$

For the next two terms I find

$$+\frac{\pi k^4b^4}{512}\,[(1+4\cos^2\alpha)(1-4\gamma-4\log\tfrac{1}{4}ikb)$$
$$+3\sin^4\alpha+\tfrac{1}{3}\cos^4\alpha+6\sin^2\alpha\cos^2\alpha]$$
$$+\frac{\pi k^6b^6}{2^2.4^2.6}[(\tfrac{1}{16}+\tfrac{3}{4}\cos^2\alpha+\tfrac{1}{2}\cos^4\alpha)(\gamma+\log\tfrac{1}{4}ikb-\tfrac{2}{3})$$
$$+\frac{157}{8^2.15}\cos^6\alpha-\frac{13}{8^2.3}\cos^4\alpha\sin^2\alpha-\frac{15}{8^2}\cos^2\alpha\sin^4\alpha-\frac{7}{8^2.3}\sin^6\alpha]. \qquad (90)$$

When $\cos\alpha = 0$, or ± 1, the calculation is simpler. Thus, when $\cos\alpha = 0$,

$$-\frac{1}{\pi}\frac{d\psi}{dx} = 1+\frac{k^2b^2}{4}\left(\gamma+\log\frac{ikb}{4}-1\right)-\frac{k^4b^4}{128}\left(\gamma+\log\frac{ikb}{4}-1\right)$$
$$+\frac{k^6b^6}{6.4^5}\left(\gamma+\log\frac{ikb}{4}-\frac{5}{4}\right)-\frac{5k^8b^8}{9.4^9}\left(\gamma+\log\frac{ikb}{4}-\frac{22}{15}\right); \qquad (91)$$

and when $\cos\alpha = \pm 1$,

$$-\frac{1}{\pi}\frac{d\psi}{dx} = 1+\frac{k^2b^2}{4}\left(\gamma+\log\frac{ikb}{4}\right) -\frac{k^4b^4}{512}\left\{20\left(\gamma+\log\frac{ikb}{4}\right)-\frac{16}{3}\right\}+\frac{k^6b^6}{6\,.\,4^5}\left\{21\left(\gamma+\log\frac{ikb}{4}\right)-\frac{683}{60}\right\} -\frac{k^8b^8}{9\,.\,4^9}\left\{429\left(\gamma+\log\frac{ikb}{4}\right)-329\right\}, \tag{92}$$

the last term, deduced from h_{14}, h_{16}, being approximate.

For the values of $-\pi^{-1}d\psi/dx$ we find from (91), (90), (92) for $kb = \frac{1}{2}, 1, \sqrt{2}, 2$:—

Table V.

	$kb = \frac{1}{2}$.	$kb = 1$.	$kb = \sqrt{2}$.	$kb = 2$.
$\cos\alpha = 0$	$0{\cdot}8448+0{\cdot}0974\,i$	$0{\cdot}5615+0{\cdot}3807\,i$	$0{\cdot}3123+0{\cdot}7383\,i$	$0{\cdot}0102+1{\cdot}3809\,i$
$\cos^2\alpha = \frac{1}{2}$	$0{\cdot}8778+0{\cdot}0958\,i$	$0{\cdot}6998+0{\cdot}3583\,i$	—	$0{\cdot}518\ +1{\cdot}129\,i$
$\cos^2\alpha = 1$	$0{\cdot}9108+0{\cdot}0944\,i$	$0{\cdot}8353+0{\cdot}3364\,i$	$0{\cdot}8587+0{\cdot}5783\,i$	$1{\cdot}020\ +0{\cdot}861\,i$

These numbers correspond to the value of Ψ expressed in (82).

We have now, in pursuance of our method, to seek a second solution with another form of Ψ. The first which suggests itself with $\Psi = 1$ does not answer the purpose. For (81) then gives as the leading term

$$-\frac{d\psi}{dx} = \left[\frac{y-\eta}{(y-\eta)^2+x^2}\right]_{-b}^{b} = \frac{2b}{b^2-\eta^2}, \tag{93}$$

becoming infinite when $\eta = \pm b$.

A like objection is encountered if $\Psi = b^2-y^2$. In this case

$$-\frac{d\psi}{dx} = 2\int\{(y-\eta)+\eta\}\frac{(y-\eta)\,dy}{(y-\eta)^2+x^2}.$$

The first part gives $4b$ simply when x becomes zero. And

$$2\int\frac{(y-\eta)\,dy}{(y-\eta)^2+x^2} = \log\frac{(b-\eta)^2+x^2}{(b+\eta)^2+x^2};$$

so that
$$-\frac{d\psi}{dx} = 4b+2\eta\log\frac{b-\eta}{b+\eta}, \tag{94}$$

becoming infinite when $\eta = \pm b$.

So far as this difficulty is concerned we might take $\Psi = (b^2-y^2)^2$, but another form seems preferable, that is

$$\Psi = b^{-2}(b^2-y^2)^{3/2}. \tag{95}$$

With the same notation as was employed in the treatment of (82) we have

$$-\frac{d\psi}{dx} = 3\int_0^{\pi}\frac{\cos\theta\,(\cos\theta-\cos\alpha)\,d\theta}{(\cos\theta-\cos\alpha)^2+x'^2}-3\int_0^{\pi}\frac{\cos^3\theta\,(\cos\theta-\cos\alpha)}{(\cos\theta-\cos\alpha)^2+x'^2}d\theta.$$

The first of these integrals is that already considered in (83). It yields 3π. In the second integral we replace $\cos^3\theta$ by $\{(\cos\theta-\cos\alpha)+\cos\alpha\}^3$, and we find, much as before, that when $x'=0$

$$\int_0^\pi \frac{\cos^3\theta\,(\cos\theta-\cos\alpha)\,d\theta}{(\cos\theta-\cos\alpha)^2+x'^2}=\pi\left(\tfrac{1}{2}+\cos^2\alpha\right). \tag{96}$$

Thus altogether for the leading term we get

$$-\frac{d\Psi}{dx}=3\pi\left(\tfrac{1}{2}-\cos^2\alpha\right)=3\pi\left(\tfrac{1}{2}-\eta^2/b^2\right). \tag{97}$$

This is the complete solution for a fluid regarded as incompressible. We have now to pursue the approximation, using a more accurate value of D than that ($\log r$) hitherto employed.

In calculating the next term, we have the same values of D and $r^{-1}d\mathrm{D}/dr$ as for (88); and in place of that equation we now have

$$-\frac{1}{k^2b^2}\frac{d\Psi}{dx}=\frac{3\pi}{16}\left(\gamma+\log\frac{ikb}{4}+\frac{1}{2}\right)$$
$$+\int_0^\pi d\theta\left[\tfrac{5}{8}\sin^4\theta-\tfrac{3}{4}\sin^2\theta+\tfrac{1}{2}\sin^2\theta\cos\theta\cos\alpha\right]\log\left\{\pm 2\left(\cos\theta-\cos\alpha\right)\right\}. \tag{98}$$

The integral may be transformed as before, and it becomes

$$4\int_0^{\frac{1}{2}\pi}d\phi\log\left(2\sin\phi\right)\left[\tfrac{5}{8}\left(\sin^4 2\phi\cos^4\alpha+6\sin^2 2\phi\cos^2 2\phi\sin^2\alpha\cos^2\alpha\right.\right.$$
$$\left.+\cos^4 2\phi\sin^4\alpha\right)-\tfrac{3}{4}\left(\sin^2 2\phi\cos^2\alpha+\cos^2 2\phi\sin^2\alpha\right)$$
$$\left.+\tfrac{3}{2}\cos\alpha\cos 2\phi\left\{\sin^2\alpha\cos\alpha+\sin^2 2\phi\left(\cos^3\alpha-3\sin^2\alpha\cos\alpha\right)\right\}\right]. \tag{99}$$

The evaluation could be effected by expressing the square bracket in terms of powers of $\sin^2\phi$, but it may be much facilitated by use of two lemmas.

If $f(\sin 2\phi, \cos^2 2\phi)$ denote an integral function of $\sin 2\phi$, $\cos^2 2\phi$,

$$\int_0^{\frac{1}{2}\pi}d\phi\log\left(2\sin\phi\right)f\left(\sin 2\phi,\cos^2 2\phi\right)=\int_0^{\frac{1}{2}\pi}d\phi\log\left(2\cos\phi\right)f\left(\sin 2\phi,\cos^2 2\phi\right)$$
$$=\tfrac{1}{2}\int_0^{\frac{1}{2}\pi}d\phi\log\left(2\sin 2\phi\right)f\left(\sin 2\phi,\cos^2 2\phi\right)=\tfrac{1}{2}\int_0^{\frac{1}{2}\pi}d\phi\log\left(2\sin\phi\right)f\left(\sin\phi,\cos^2\phi\right), \tag{100}$$

in which the doubled angles are got rid of.

Again, if m be integral,

$$\int_0^{\frac{1}{2}\pi}d\phi\sin^{2m}2\phi\cos 2\phi\log\left(2\sin\phi\right)$$
$$=\frac{1}{4m+2}\int\log\left(2\sin\phi\right)d\sin^{2m+1}2\phi$$
$$=-\frac{1}{4m+2}\int_0^{\frac{1}{2}\pi}\sin^{2m}2\phi\left(1+\cos 2\phi\right)d\phi$$
$$=-\frac{1}{4m+2}\int_0^{\frac{1}{2}\pi}\sin^{2m}2\phi\,d\phi=-\frac{1}{4m+2}\int_0^{\frac{1}{2}\pi}\sin^{2m}\phi\,d\phi$$
$$=-\frac{1}{4m+2}\,\frac{2m-1\,.\,2m-3\ldots 1}{2m\,.\,2m-2\ldots 2}\,\frac{\pi}{2}. \tag{101}$$

For example, if $m = 0$,

$$\int_0^{\frac{1}{2}\pi} d\phi \cos 2\phi \log(2\sin\phi) = -\frac{\pi}{4}, \tag{102}$$

and ($m = 1$)

$$\int_0^{\frac{1}{2}\pi} d\phi \sin^2 2\phi \cos 2\phi \log(2\sin\phi) = -\frac{\pi}{24}. \tag{103}$$

Using these lemmas, we find

$$\begin{aligned}(99) = {} & 5h_4(\cos^4\alpha - 6\cos^2\alpha\sin^2\alpha + \sin^4\alpha) \\ & + h_2(30\cos^2\alpha\sin^2\alpha - 10\sin^4\alpha - 3\cos^2\alpha + 3\sin^2\alpha) \\ & - \tfrac{1}{4}\pi\cos^2\alpha(\cos^2\alpha + 3\sin^2\alpha):\end{aligned}$$

and thence, on introduction of the values of h_2, h_4, for the complete value to this order of approximation,

$$\begin{aligned}-\frac{d\psi}{dx} = {} & 3\pi\left(\frac{1}{2} - \cos^2\alpha\right) + \pi k^2 b^2 \left[\frac{3}{16}\left(\gamma + \frac{1}{2} + \log\frac{ikb}{4}\right)\right. \\ & \left. - \frac{1}{64}(5\cos^4\alpha + 18\cos^2\alpha\sin^2\alpha + 21\sin^4\alpha)\right].\end{aligned} \tag{104}$$

To carry out the calculation to a sufficient approximation with the general value of α would be very tedious. I have limited myself to the extreme cases $\cos\alpha = 0$, $\cos\alpha = \pm 1$. For the former, we have

$$\begin{aligned}-\frac{1}{\pi}\frac{d\psi}{dx} = {} & \frac{3}{2} + \left(\gamma + \log\frac{ikb}{4}\right)\left\{\frac{3k^2b^2}{16} - \frac{k^4b^4}{256} + \frac{k^6b^6}{2^2.4^4.256}\right\} \\ & - \frac{15k^2b^2}{64} + \frac{7k^4b^4}{6.256} - \frac{11k^6b^6}{4^3.256.8},\end{aligned} \tag{105}$$

and for the latter

$$\begin{aligned}-\frac{1}{\pi}\frac{d\psi}{dx} = {} & -\frac{3}{2} + \left(\gamma + \log\frac{ikb}{4}\right)\left\{\frac{3k^2b^2}{16} - \frac{7k^4b^4}{16.16} + \frac{33k^6b^6}{4.16.16.16} - \frac{143k^8b^8}{24.16^4}\right\} \\ & - \frac{5k^2b^2}{64} + \frac{41k^4b^4}{16.64.15} + \frac{1069k^6b^6}{16.3.70\ 64.64} - \frac{41309k^8b^8}{16^5.9.420} \\ & + \frac{3k^2b^2}{32} + \frac{7k^4b^4}{4.16.16} - \frac{11k^6b^6}{2.16^3} + \frac{3289k^8b^8}{16^5.36}.\end{aligned} \tag{106}$$

From these formulæ the following numbers have been calculated for the value of $-\pi^{-1}d\psi/dx$:—

Table VI.

	$kb = \frac{1}{2}$.	$kb = 1$.	$kb = \sqrt{2}$.	$kb = 2$.
$\cos\alpha = 0$	$1{\cdot}3716 + 0{\cdot}0732\,i$	$1{\cdot}1215 + 0{\cdot}2885\,i$	$0{\cdot}8824 + 0{\cdot}5653\,i$	$0{\cdot}5499 + 1{\cdot}0860\,i$
$\cos\alpha = \pm 1$	$-1{\cdot}5634 + 0{\cdot}0710\,i$	$-1{\cdot}6072 + 0{\cdot}2546\,i$	$-1{\cdot}5698 + 0{\cdot}4401\,i$	$-1{\cdot}3952 + 0{\cdot}6567\,i$

They correspond to the value of Ψ formulated in (95).

Following the same method as in case (i), we now combine the two solutions, assuming

$$\Psi = \mathrm{A}\sqrt{(b^2-y^2)}+\mathrm{B}b^{-2}(b^2-y^2)^{3/2}, \tag{107}$$

and determining A and B so that for cos α = 0 and for cos = ±1, $d\psi/dx$ shall be equal to $-ik$. The value of ψ at a distance in front is given by (76), in which

$$ik\int \Psi\, dy = \frac{\pi\,.\,ikb^2}{2}\left(\mathrm{A}+\frac{3}{4}\mathrm{B}\right). \tag{108}$$

We may take the modulus of (108) as representing the transmitted vibrations, in the same way as the modulus of (67) represented the transmitted vibration in case (i).

Using p, q, r, s, as before, to denote the tabulated complex numbers, we have as the equations to determine A and B,

$$\mathrm{A}p+\mathrm{B}q = \mathrm{A}r+\mathrm{B}s = ik/\pi, \tag{109}$$

so that

$$ik\int \Psi\, dy = -\frac{k^2b^2}{2}\,\frac{s-q+\frac{3}{4}(p-r)}{ps-qr}. \tag{110}$$

For the second fraction on the right of (110) and for its modulus we get in the various cases

$kb = \frac{1}{2}$,	$1{\cdot}1470-0{\cdot}1287i$,	$1{\cdot}1542$,
$kb = 1$,	$1{\cdot}1824-0{\cdot}6986i$,	$1{\cdot}3733$,
$kb = \sqrt{2}$,	$0{\cdot}6362-1{\cdot}0258i$,	$1{\cdot}2070$,
$kb = 2$,	$0{\cdot}1239-0{\cdot}7303i$,	$0{\cdot}7407$.

And thence (on introduction of the value of kb) for the modulus of (110) representing the vibration on the same scale as in case (i).

Table VII.

kb.	Modulus.
½	0·1443
1	0·6866
√2	1·2070
2	1·4814

These are the numbers used in the plot of Curve B, fig. 1. When kb is much smaller than ½, the modulus may be taken to be $\frac{1}{2}k^2b^2$. When kb is large the modulus approaches the same limiting form as in case (i).

This curve is applicable to electric, or luminous, vibrations incident upon a thin perfectly conducting screen with a linear perforation when the electric vector is *parallel* to the direction of the slit.

It appears that if the incident light be unpolarised, vibrations perpendicular to the slit preponderate in the transmitted light when the width of the slit is very small, and the more the smaller this width. In the neighbourhood of $kb = 1$, or $2b = \lambda/\pi$, the curves cross, signifiying that the transmitted light is unpolarised. When $kb = 1\frac{1}{2}$, or $2b = 3\lambda/2\pi$, the polarisation is reversed, vibrations parallel to the slit having the advantage, but this advantage is not very great. When $kb > 2$, our calculations would hardly succeed, but there seems no reason for supposing that anything distinctive would occur. It follows that if the incident light were white and if the width of the slit were about one-third of the wave-length of yellow-green, there would be distinctly marked opposite polarisations at the ends of the spectrum.

These numbers are in good agreement with the estimates of Fizeau: "Une ligne polarisée perpendiculairement à sa direction a paru être de $\frac{1}{1000}$ de millimètre; une autre, beaucoup moins lumineuse, polarisée parallèlement à sa direction, a été estimée à $\frac{1}{10000}$ de millimètre. Je dois ajouter que ces valeurs ne sont qu'une approximation; elles peuvent être en réalité plus faibles encore, mais il est peu probable qu'elles soient plus fortes. Ce qu'il y a de certain, c'est que la polarisation parallèle n'apparaît que dans les fentes les plus fines, et alors que leur largeur est bien moindre que la longueur d'une ondulation qui est environ de $\frac{1}{2000}$ de millimètre." It will be remembered that the "plane of polarisation" is perpendicular to the electric vector.

It may be well to emphasize that the calculations of this paper relate to an aperture in an *infinitely thin* perfectly conducting screen. We could scarcely be sure beforehand that the conditions are sufficiently satisfied even by a scratch upon a silver deposit. The case of an ordinary spectroscope slit is quite different. It seems that here the polarisation observed with the finest practicable slits corresponds to that from the less fine scratches on silver deposits.

Experiments on the Temperature Coefficient of a Kew Collimator Magnet.

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It is usually assumed that the relation between the moment m_t of a collimator magnet used in determining the horizontal component of the earth's magnetic field is dependent on the temperature, the relation being given by the equation $m_t = m_0 (1-qt-q't^2)$. The evidence, however, upon which this assumption is based not appearing conclusive, the writer was led to make an independent investigation of the subject, and the present paper is an account of the experiments carried out with that object on a Kew collimating magnet of the ordinary type about 20 years old.

One of the difficulties in any magnetometer observations arises from the variability of the earth's field. Variations may be either those of a widespread nature, such as are generally dealt with under the name of diurnal variation, or those of purely local origin, due to the proximity of electric trams, dynamo-electric machinery, electric mains, or like causes Among those disturbances we may include those arising from earth currents, since these currents, to whatever cause they may be due, are often of much more considerable magnitude that is usually suspected.

It is therefore necessary to eliminate the errors which such disturbances might produce. The method of attaining this end, which suggested itself to the writer, is the use of what may be called a compensating magnetometer. The principle of the method is simple. Let A and B be two plane mirrors. Then, if a ray of light falling on one of these be reflected on to the other in the way indicated in the diagram (fig. 1), the direction of the emergent ray will make with that of the incident ray a certain angle dependent on the angle between the planes of the mirrors. If, now, each of the mirrors be rotated through the same small angle in the same sense, the deviation of the ray brought about by the first mirror will be corrected by the second, and the emergent ray will still form the same angle with the ray incident on the first mirror. Hence, if the ray comes from a very distant scale, and is received in a telescope, there is no displacement of the image of the scale in the field of view.

In practice it is often inconvenient to have the scale at a great distance, and to overcome this difficulty a collimator may be used, having a scale at the focus of the collimating lens. A more convenient device, however, is to use an ordinary scale at a moderate distance. But in this case there will be a movement of the image of the scale in the field of view, depending on the distance between the mirrors, and, to secure absence of such movement, the mirror B must be made to move through a slightly greater angle than the mirror A. If A and B be the mirrors attached to two magnetometers, this end can be attained by slightly weakening the controlling field of the magnetometer B by the use of a small subsidiary magnet so arranged as to weaken the field without altering its direction, in a manner to be described later. In this way the image of a scale viewed with a telescope in the manner indicated may be made to remain stationary, though the direction of the field change considerably.

It is assumed that the disturbing force may be regarded as a second uniform field superposed on the general field of the earth. But it is useful to note that if the disturbing field be not uniform (as in the case of a neighbouring dynamo), it is still possible to arrange the strength of the field at the compensating magnetometer in such a way as to eliminate disturbance, provided the relative magnitudes of the disturbing field at the two magnetometers remain constant. But if the field be thus arranged to compensate for a non-uniform field, which varies in a given ratio at the two magnetometers respectively, it will not be such as to compensate for a uniform disturbing field. It is, for instance, possible to compensate for the effect of a dynamo at a distance of, say, 10 metres, but not at the same time for electric trams at a distance of 400 metres.

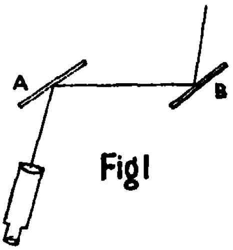

Fig I

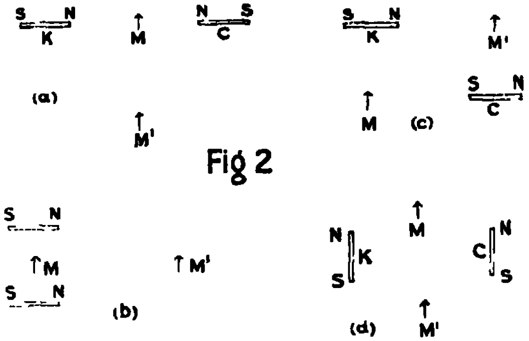

Fig 2

In the present experiments compensation was made for uniform disturbing fields, thus eliminating the effect of the trams and of the diurnal change. Experiments were suspended while dynamos close at hand were being used, though the disturbances due to those were very greatly diminished.

Arrangement of Magnets and Magnetometers.—A differential method was used, in which the effect of the magnet to be tested was balanced by means of a compensating magnet at ordinary temperature. Several dispositions of the apparatus were tried, which will be understood from the accompanying figure (fig. 2), where K and C represent the Kew magnet and compensating magnet respectively, and M and M′ the primary and compensating magnetometers.

Of these (*a*) was most satisfactory and was used exclusively in the later work, so that the description given must be taken to apply to this case unless otherwise stated.

Heating Arrangements.—The Kew magnet was contained in a brass tube, being fixed therein by its middle point by means of a collar of brass provided with two projecting teeth at the bottom and a central screw at the top, as shown in section at P (fig. 3). The collar was brazed to the brass tube at the middle of its length, an aperture B being left above the screw to allow the latter to be screwed up when the magnet had been inserted in its place, by means of a gauge bar, through the open end A of the tube. A short tube from this aperture to the exterior was closed with an indiarubber bung.

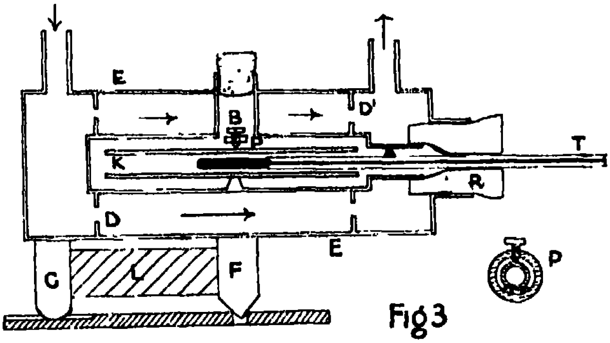

Fig 3

This magnet tube was fixed by means of two perforated annuli of brass, D and D′, in the middle of a large tube EE, which served as a water jacket, through which water could be allowed to flow by means of inlet and outlet tubes as indicated by the arrows. Brazed on the underside of the outer tube at the middle point was a short rod of brass (F) with a conical point. At G two other hemispherical feet were attached. These three feet rested on a brass plate which had a hole to receive the point of the cone F and a V groove to take the hemispherical end of one foot G, the end of the third foot resting on the plane surface of the plate. This elaborate arrangement was necessary to secure that the centre of the magnet should neither approach nor recede from the magnetometer in the course of heating or cooling, for an extremely small movement would entirely mask the true nature of the effect to be observed. The water jacket was covered with thick felt; and a lump of lead (L) was fixed between the feet for greater stability. The brass plate was cemented down to a slate slab on which the magnetometer and compensating magnet stood.

As an illustration of the necessity for elaborate precautions to avoid small changes of distance, it may be mentioned that the tilting of the floor due to change of position of the observer may be quite sufficient to produce an appreciable change of scale reading. In fact the changes in humidity and temperature caused minute tilting of the wooden table and wooden magnetometers at first used, thereby producing irregularities which seemed inexplicable. These troubles, however, were overcome by building up a table made of a slate slab on masonry supports standing on the concrete floor, from which the wooden blocks had been removed, and by making the magnetometers of brass.

The water supply from the main passed through a gas heater on its way to the water jacket and the temperature of the latter could be adjusted to any value between about 9° C. and 60° C., and kept constant to about 0·01° C.

The temperature of the magnet was given by the thermometer T which projected into the middle of the magnet through the rubber bung R. The range of temperature used in most of the experiments was about 10° C. to 35° C., *i.e.* about such variations as a Kew magnet in ordinary use, and occasionally handled, might be subjected to. In some of the experiments however, the range was considerably greater.

Compensating Magnet.—The compensating magnet was contained in a brass tube fitted into a brass box, in which the tube was surrounded by about a litre of water. In this way the temperature of the compensating magnet changed very slowly with the change of the room temperature.

It was necessary, as will be seen later, that the compensating magnet should be of as nearly as possible the same length and moment as the Kew magnet. To secure this, the magnet was built up of a number of thin magnetised rods, each of the same length as the Kew magnet, the number being chosen to give approximately the same moment as that of the Kew magnet. These rods were arranged in the form of a tube inside a brass tube and a thermometer projected into the middle of the compound tubular magnet thus formed.

Magnetometers.—Each of these consisted of a box with three sides of glass, the framework and the remaining side being of brass. This last side had a large circular opening. When the magnetometers were in position, these two apertures faced one another and were connected by means of a cardboard tube covered with felt, so that a beam of light could pass from the mirror of the one instrument to that of the other without traversing any unnecessary glass on the way. The mirrors were sextant mirrors about $2{\cdot}5 \times 2$ cm., silvered on both sides. Each was fitted with eight small magnetised needles about 1 cm. long, mounted on a small slab of cork through which passed a thin copper wire depending centrally from the frame of the mirror. By this means the needles could be turned to any desired orientation with respect to the mirrors. The copper wire was continued below the needles and was bent into the form of a horizontal ring about 1 cm. beneath them. This ring dipped into a dash-pot of oil, the size of the ring being such as to make the motion of the magnetometers very nearly dead-beat. The mirror and needles were suspended with a single fibre of cocoon silk about 10 cm. long.

Adjustment.—The two magnetometers were placed in the required position in the same N.S. line. The mirror and telescope were then adjusted so that the scale was seen by reflection in both mirrors as shown in fig. 4. For making the final adjustment it was necessary to be able to superpose on each of the magnetometers equal fields transverse to that of the earth; for this purpose a long bar magnet was placed at a distance of about 5 metres on the line bisecting the distance between the magnetometers at right angles. By means of telescopes viewing a scale by reflection from the backs of the mirrors the position of the bar magnet was adjusted so that on rotation of the magnet through 180° about a vertical axis, equal deflections were produced in the two magnetometers. The position of the magnet was then marked and the magnet removed.

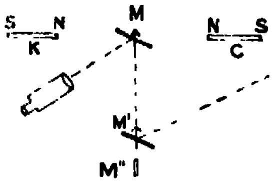

Fig 4

The Kew magnet was next placed in position to the W. of the primary magnetometer so as to lie in an E.W. line passing through the centre of that magnetometer, but so as not to produce any deflection of the compensating magnetometer. The compensating magnet was now brought into position to restore the primary magnetometer to its original direction, while at the same time giving no deflection of the compensating magnetometer. This was rendered simple by the equality of its moment and length with those of the Kew magnet.

On now bringing into position the disturbing bar magnet, the two magnetometers, being in controlling fields of unequal magnitudes, were deflected through different angles and the image of the scale seen by reflection in *both* mirrors moved.

In the case represented in the diagram (fig. 4), the controlling field at M′ is too small. A small subsidiary magnet, M″, of steel wire, about 3 cm.

long, fixed in a brass support, was therefore brought to a suitable position S. of the compensating magnetometer to give an increase in magnitude of the controlling field (without change in direction), so that on rotating the disturbing magnet no deflection was observed in telescope T. In this way the deflections due to the disturbing magnet were reduced to less than 1/400 of that which would have been given without the compensating device.

It is evident that if the moments of K and C remain constant, small changes in the direction of the earth's field will not alter the scale reading. But if the temperature vary, the moments of the two magnets will in general vary to differing extents. It is necessary, therefore, to determine the change of scale reading due to each degree change of temperature of the compensating magnet, the Kew magnet being kept meanwhile at constant temperature. This was done separately for each arrangement of the apparatus.

Course of an Experiment.—The water was turned on through the water jacket of the K magnet and when the temperature indicated by the thermometer remained steady the scale was read and the temperatures of both magnets were taken. The gas was now lighted in the heater through which the water passed on its way to the magnet. The temperature of the magnet could thus be gradually raised to any desired temperature up to about 60° by adjusting the gas tap. Readings of scale and thermometers were taken at suitable intervals of temperature; the temperature of the magnet being allowed to become steady before taking a reading. To avoid rapid fluctuations in temperature the water after leaving the heater passed through a spiral of metal tube immersed in a vessel of water, to serve as a sort of temperature flywheel. The temperature of the magnet thus could not be suddenly changed.

Value of $\delta m/m$.—So far we have dealt with changes in the moment for a given change in temperature. It is necessary to know the ratio of such changes to the original value of the moment. Several ways of doing this were tried, but the following proved most satisfactory. The primary magnetometer was fitted with a coil consisting of two single turns of insulated wire, one on each side of the needle, the common axis of the turns passing through the centre of the needle system (as seen in fig. 6), so that, when an electric current passed, a field was produced perpendicular to the horizontal component of the earth's field and in the same direction as that due to the Kew magnet. The Kew magnet and compensating magnet having been adjusted in position as already described, the Kew magnet was removed and a current was sent through the coil so as to restore the needle to its original position. (The effect of the coil on the compensating magnetometer was balanced by means of a single turn of wire in series with the coil, not shown in the diagram.) The magnitude of the current C was measured by means of a potentiometer.

The current was then stopped and the Kew magnet was replaced in position and heated through any desired range of temperature, the small current δC necessary to restore the needle to zero position being determined. It was assumed that $\delta m/m$ was equal to $\delta C/C$. In this way the value of each scale division could be determined in terms of the total effect due to the Kew magnet alone. In some of the experiments the results were obtained by means of the current at each temperature, in others by observing the scale deflection and deducing the ratio $\delta m/m$ from the value of each division determined at the beginning of the experiment. The advantage of this method lies in the elimination of the uncertainties introduced by torsion of the suspending fibre. Separate experiments devised for the purpose showed that the effect of the current in the coil upon the Kew magnet and compensating magnet was negligible.

Results.—The moment of the magnet is not simply a function of the temperature. The relation is complicated by the fact that time enters into it. Moreover, the moment at any given temperature depends on the previous history of the magnet; *e.g.*, in general, the moment at a given temperature depends to some extent upon whether that temperature was preceded by a higher or a lower temperature and also upon the extreme temperature to which it has immediately previously been subjected.

The general effect may be illustrated by reference to two curves shown in fig. 5. These two curves are for two consecutive temperature cycles, the second covering a greater range than the first. The arrows indicate the branches of the curves corresponding to rising and falling temperatures respectively. The range of temperature in these curves is somewhat greater than in the majority of cases investigated, and in consequence the effects to be noticed are considerably greater, and thereby made clearer. The dotted lines are straight lines.

It will be noted that the curve for falling temperature in each case lies below that for rising temperature. The curve AB is represented by the equation

$$m_t = m_{17}\{1-3{\cdot}292\times10^{-4}(t-17)-1{\cdot}15\times10^{-6}(t-17)^2\}.$$

The moment at 17° C. has been taken for convenience as 1000.

In general, if the cycle has been performed at about the same rate throughout, the sagitta of the cooling branch is less than that of the warming branch. In fact, the cooling branch is often indistinguishable from a straight line, the actual shape depending largely upon the rate of cooling at different parts of the range of fall of temperature. If the first part of the fall is made rapidly and the last part slowly the curvature of the branch may be reversed, so as to be concave upwards.

It will be seen that in the case illustrated there is a subpermanent loss

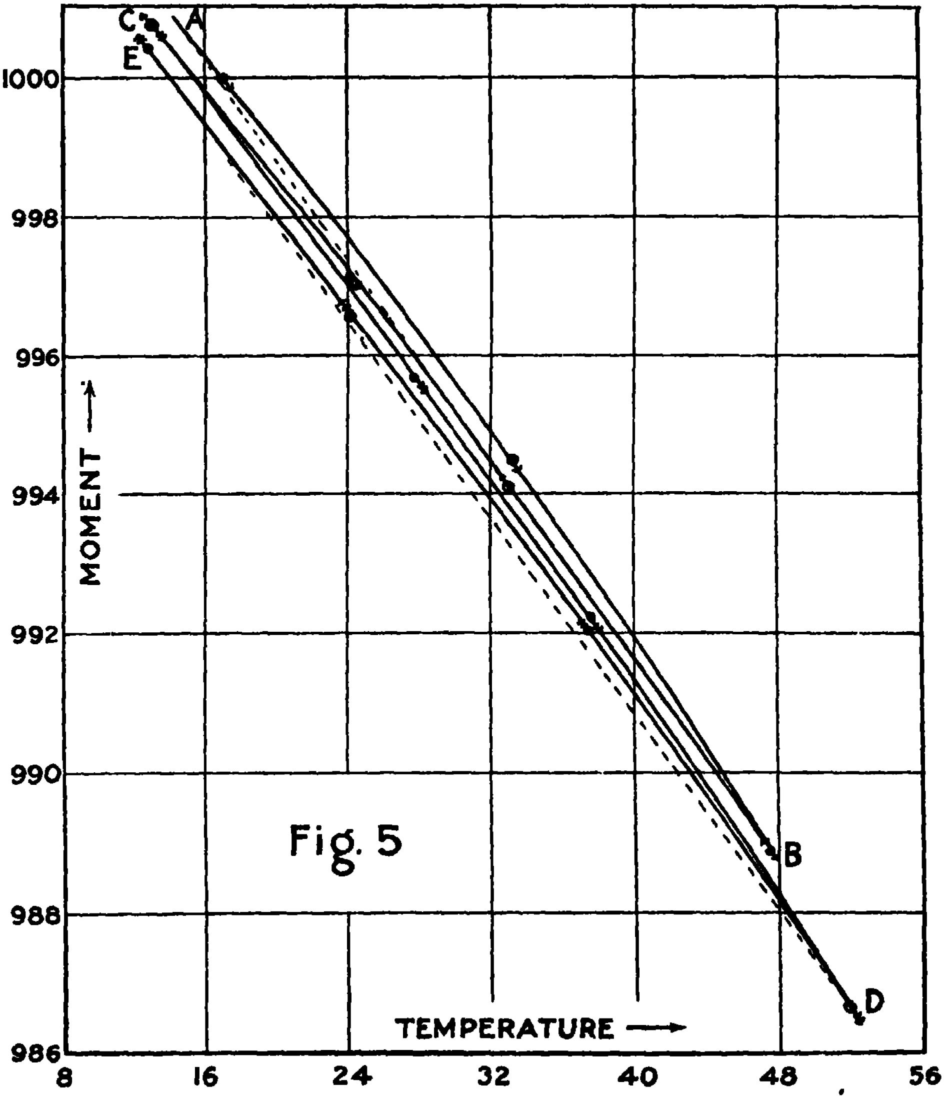

Fig. 5

of moment on cooling to the final temperature in each cycle, the loss due to the second being very slightly less than that due to the first. But if the second cycle had been for the same range of temperature (instead of a greater) the second loss would have been considerably less than the first.

For the experiments show that this subpermanent loss is dependent on the highest temperature reached.

In successive cycles of the same range this subpermanent loss rapidly diminishes, so that if, for example, we take three cycles in quick succession, the loss for the second is less than that for the first, while that for the third is less than that for the second.

The subpermanent loss, however, gradually disappears after the cycle is ended if the temperature is kept constant. Thus, in the case shown, after a rest of about 48 hours, the finishing point E would have risen so as to lie very nearly on the original curve AB, though it would still be slightly below.

In fact, the experiments show that it is highly probable that any cycle results in a very small permanent loss of moment, even if the range be only one of a few degrees centigrade; but the higher the extreme temperature the greater the permanent loss.

In the case shown the curve CD lies entirely below the curve BC, but this is not always so; the curve for the second heating may lie largely above that for the first cooling, especially if the interval of time between the two cycles be somewhat long (say two or three hours).

To illustrate the gradual recovery of the subpermanent loss the result of a cycle in which the range of temperature was from 7° to 31° C. may be quoted. At the end of the cycle the moment had at 7° C. the value which it previously had at 7·9° C. on the warming branch of the curve. But in 48 hours it had recovered to such an extent that at 7° C. its value was that which it previously had at 7·1° C.

If the magnet has been heated to, say, 60° C. and cooled quickly to, say, 15° C. and then quickly heated again to, say, 25° C. the recovery is facilitated, so that at the end of the second cycle the moment may be greater than at the beginning of that cycle, though less than at the beginning of the previous one.

In general we may say that the subpermanent effect of a cycle is always greater for the first cycle after a period of rest of several days than for succeeding cycles following at short intervals, the range of temperature in each case being the same.

In fact there is a striking analogy between this effect and the permanent lengthening of a wire which has been stretched with a load far below that required to reach the elastic limit. For it has been shown that a wire does not accurately recover its length after being stretched with a comparatively small load and this subpermanent residual stretch is greater for the first load after a period of rest than for succeeding loads following at short intervals. This fact suggests that part at least of the effect of a change of temperature on the moment of a magnet may be ascribed to the same kind of action as occurs in the stretching of a wire, *i.e.* to some change in the relative positions of the crystals of which the steel is composed. Such a change would occur if the crystals had a coefficient of expansion slightly different from that of the matrix in which they were embedded, with a consequent minute amount of rupture on heating; and the gradual recovery with time after cooling would be accounted for by the gradual growing together again of the crystals. There can be little doubt that the magnetic properties of the steel depend to some extent on the crystalline structure of the metal.

It may be noted that permanent effects on the moment of the magnet tend to be masked by permanent effects of changes of temperature on the compensating magnet, but if the latter is kept at a fairly constant temperature the compensating device enables the experiments to be carried on continuously for months without appreciable change of zero.

Effect of the Magnetic Field, in which the Magnet lies, on the Temperature Coefficient.—Experiments with different arrangements (*a*) (*b*) (*c*) (*d*), fig. 2, suggested that the temperature coefficient might be slightly affected by the field in which the magnet lay.

To test this point the primary magnetometer alone was used. This magnetometer was supported on a vertical rod attached to a fixed horizontal slab. The Kew magnet was fixed on a second slab which was capable of rotating in a horizontal plane about the vertical rod. The Kew magnet was first laid in an E.W. direction, as indicated at K, fig. 6, in such a position as to produce no deflection of the magnetometer. The slab was then rotated through 90° so as to bring the magnet to position K′, when its field would of course be perpendicular to that of the earth. The compensating magnet was placed at C, fig. 6, to restore the magnetometer to zero; the Kew magnet was then removed, and the current required in the coil to restore the magnetometer to zero once more was observed. The Kew magnet was then replaced at K′ and heated through a certain range of temperature and the small current which was necessary again to restore the magnetometer was measured. The whole experiment was then repeated with the Kew magnet reversed, end for end, *i.e.* with its S.-seeking pole to the northward. Thus the mean coefficient over a given range of temperature could be found when the magnet was lying in fields differing by about 2 H. The results showed that for the magnet under investigation the temperature coefficient is not sensibly affected by changes of field of the order of H.

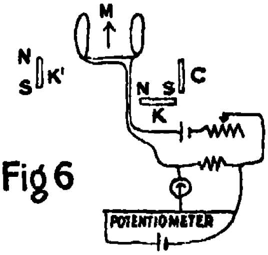

Fig 6

Conclusions.

We may now give a summary of the conclusions to which the experiments lead :—

(1) For a steady rise of temperature, the relation between the moment m_t at a temperature t° above some standard temperature, O, may be approximately represented by an equation of the form

$$m_t = m_0(1-qt-q't^2),$$

where q and q' are constants, and for a subsequent steady fall a similar equation holds, but with different constants.

(2) If the rise and fall of temperature be not steady, the relation cannot be represented by any such simple equation.

(3) There is always, even for a change of temperature of only a few degrees, a residual weakening of the magnet, which diminishes with time, if kept at constant temperature, until after the lapse of about 24 hours the original value is very nearly (though perhaps never perfectly) regained.

(4) It appears that it is easy to over-rate the degree of accuracy with which the moment of a collimator magnet at any temperature can be deduced from that at some other temperature, the application of the ordinary quadratic formula being likely to give an apparent degree of accuracy which is quite illusory.

Perhaps the following way of dealing with the question would be fairly satisfactory. Suppose the magnet is generally to be used at temperatures in the neighbourhood of 15° C. Let the magnet be heated to, say, 30° C., and the mean coefficient α over this range be observed. Then let it be cooled to, say, 0° C., and the mean coefficient β over this range be ascertained. Now, let us suppose that we are doing magnetometer observations, and having done the oscillation experiment at temperature θ we proceed to the deflection experiment. If now the temperature has risen to $\theta+t$, we may put for the moment

$$m_{\theta+t} = m_\theta(1-\alpha t)$$

If, on the other hand, the temperature has fallen to $\theta-t$, we may put

$$m_{\theta-t} = m_\theta(1+\beta t).$$

Probably some such method as this would lead to rather more accurate results than would be attained by the simple application of the quadratic formula. But if the collimating magnet is to be regarded as an instrument of precision its temperature must not be allowed to vary more than a few degrees, and after being handled it should not be used for some hours, as such handling may give rise to a subpermanent change of moment which will not immediately disappear. It is, moreover, necessary to take precautions to secure that the temperature of the magnet is known, especially as, in the ordinary use of a Kew magnetometer, an error of even half a degree in the estimate of the temperature is by no means impossible.

(5) For differences of field of the order of ±H the temperature coefficient is not sensibly affected by the field.

In conclusion, I wish to thank my assistant, Mr. E. Simpson, for help in construction and adjustment of apparatus throughout the work.

Note.—The principle of the compensating magnetometer may be applied to needle galvanometers, and I have constructed an instrument consisting of two galvanometers to test the utility of such an application. I have not yet had an opportunity of fully investigating its possibilities, but it seems likely that a high degree of sensitiveness may be attained with a fair immunity from effects of small local magnetic disturbances. Moreover, for a given resistance, two galvanometers with this arrangement can be made more efficient than one.

On Light-Sensations and the Theory of Forced Vibrations.

By George J. Burch, M.A., D.Sc. Oxon, F.R.S.

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A Case of Abnormal Trichromatic Colour Vision due to a Shift in the Spectrum of the Green-Sensation Curve.

By Sir W. de W. Abney, K.C.B., F.R.S., and W. Watson, D.Sc., F.R.S.

(Received June 13,—Read June 26, 1913.)

The authors have each separately dealt with the question of complete and incomplete colour-blindness caused by the absence of, or decrease in, the response to stimulation of the red or green perceiving apparatus which is functional in the case of vision. We have shown that a large number of cases of defective perception of colour are simply explained on this hypothesis. Abnormality of colour vision may also be due to a shift in, or an alteration in form of, one of the sensation curves. In the present paper we discuss the effect of one type of shift on the colour perception and give the results of a series of measurements which show that such a shift, without any alteration of form, does sometimes occur.

In a paper which appeared in the 'Proceedings of the Royal Society,'* one of us indicated how a shift, that is a displacement of the whole curve so that the maximum is displaced to a different wave-length, of one of the sensation curves could be detected by a simple spectrum test, which is as follows. When yellow light of wave-length 5760 Å.U. is mixed with blue light of wave-length 4610 in suitable proportions the mixed light looks to the normal eye exactly the same as the white light from the crater of the electric arc both in hue and brightness. If a person who has a shift in one of the sensation curves is shown this match it will not appear correct to him nor can it be made correct by any alteration in the proportions of the yellow and blue lights. There will, however, in every case be found a position of the slit through which the yellow light is obtained with which a satisfactory match can be obtained. In other words the wave-length of the light which is complementary to the blue will be different to that of normal vision.

On the other hand, where the colour perception defect is due to a deficiency of one of the sensations the observer will agree that the match made by the normal is correct, although in most cases he will also consider correct matches made when the yellow slit is moved to one or other side of the normal setting, the range being the larger the greater the defect.

In order to see why in the case of colour defect due to a deficiency in one of the sensations the normal match appears correct it is necessary to consider the sensation curves. In fig. 1 are given the sensation curves of the spectrum colours for the normal eye, the source of light being the crater of an arc with a horizontal positive carbon, *i.e.* one in which the crater directly faces the slit of the spectroscope. The sensations are given in terms of luminosity* so that the sum of the ordinates of the three curves for any wave-length is equal to the luminosity at that wave-length. Since the luminosity of the blue sensation is so small compared to the others the blue sensation curve has been plotted on a scale 100 times as great as that adopted for the red and green sensations. When considering the matches made between mixtures of different coloured lights it is, however, often convenient to adopt a different scale, namely, one in which the areas of the three sensation curves are all equal. With this scale equal ordinates of the three sensation curves correspond to a mixture which will appear to the normal eye as white. The areas of the three sensation curves on the luminosity scale are Red = 579, Green = 248 and Blue = 3·26, and these correspond to the sensation produced by the whole combined spectrum, that is by white light. If we multiply the ordinates of the green sensation curve by 579/248 or 2·21, and those of the blue sensation curve by 579/3·26 or 117, the green and blue sensation curves will have the same area as the red sensation curve. The three sensation curves plotted on this scale are shown by the full line curves in fig. 2.

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* 'Roy. Soc. Proc.,' 1912, A, vol. 87.

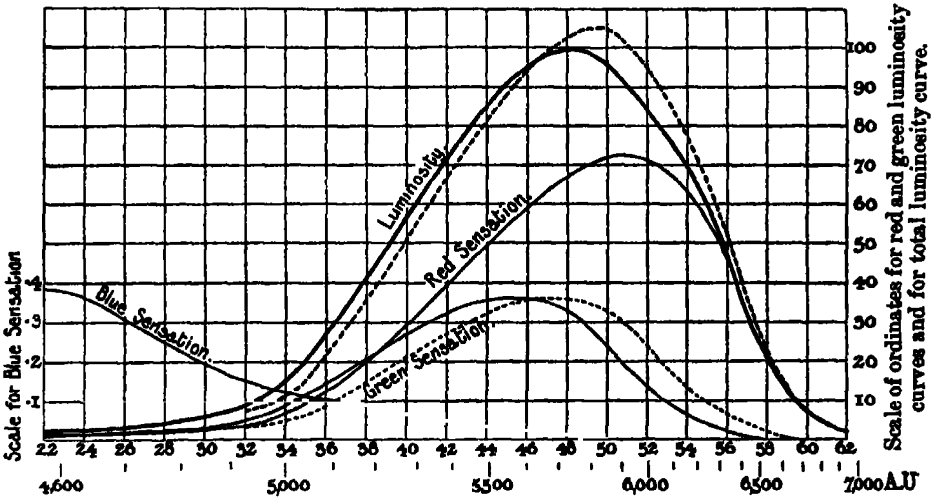

FIG. 1.—Scale of prismatic spectrum (S.S.N.), showing wave-lengths.

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* An explanation of what is meant by the luminosity of a coloured light is given on p. 404 of vol. 88 (A, 1913) of the 'Proceedings.'

Let us now consider an observer who has, say, only half the normal green sensation, so that on the luminosity scale the ordinates of his green-sensation curve will be half those for the normal curve. On the equal area scale, however, his green-sensation curve will be the same as the normal, for since the area of the green-sensation curve on the luminosity scale is now 124, to obtain the equal area scale we must multiply by 579/124 or 4·42. Hence, since the multiplier is twice as great as for the normal, the resulting curve will be the same as for the normal.

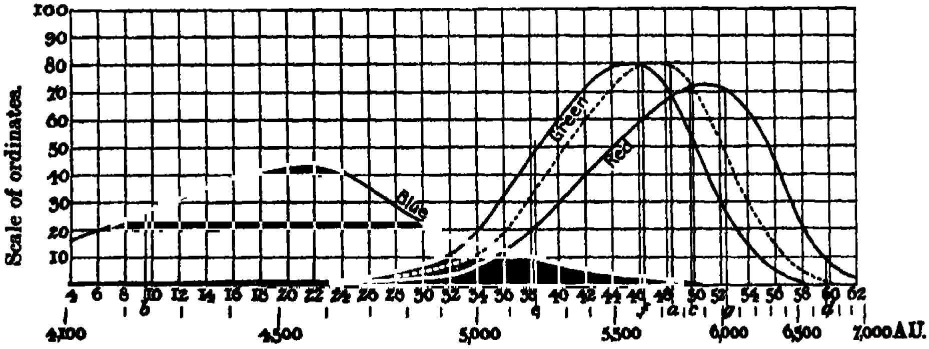

FIG. 2.—Scale of prismatic spectrum (S.S.N.), showing wave-lengths.

Now if we take a yellow at S.S.N.* 48·4 (5760 Å.U.), *i.e.* at *a* (fig. 2), and mix it with a violet at S.S.N. 9·5 (4235 Å.U.), *i.e.* at *b* (fig. 2), the width of the violet slit being 2·5 times that of the yellow, and read off the three sensations at these places from the full line curves given in fig. 2, the values in the violet being multiplied by 2·5, we get the following numbers:—

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* The values of the scale numbers given in the diagrams in terms of wave-length are as follows:—

S.S.N.	Wave-length. Å.U.	S.S.N.	Wave-length. Å.U.
62	6957	34	5002
60	6728	32	4924
58	6521	30	4848
56	6330	28	4776
54	6152	26	4707
52	5996	24	4639
50	5850	22	4578
48	5720	20	4517
46	5596	18	4459
44	5481	16	4404
42	5373	14	4349
40	5270	12	4296
38	5172	10	4245
36	5085	8	4198

Table I.

Position of slit.	Sensations.		
	Red.	Green.	Blue.
a	67·9	69·3	1·6
b	1·4	0	67·7
Sums	69·3	69·3	69·3

Since the sums for the three sensations are the same it follows that the mixture will look white to the normal eye. Further, since the curves for the person who has half the green sensation are precisely similar, the sums will be equal for him also and hence he will match the mixed colour with his own white. Similarly for any other case of colour defect, where the defect is due to a deficiency of one of the sensations, the equal areas of the sensations will be the same as those of the normal eye.

Although the person who has a defect of one of the sensations will agree with the normal match, it will be found that when making the match the position of the yellow slit can be moved some little distance from the correct position for the normal without the match becoming defective to him. This want of definiteness of the mixture required for a match when one of the colour sensations is defective can be illustrated by fatiguing the normal eye (say) with red so that temporarily the red sensation is defective. This effect is illustrated in the following matches made by one of us. In each case white was matched by a mixture of red, green and violet light by altering the width of the slits through which the coloured light proceeded. In the case of both the unfatigued and the fatigued eye not only was a correct match made but also one when the green slit was so much reduced that the deficiency in green was just observable and one where this slit was so much opened that the excess of green was just perceptible, the red slit being kept at a constant width throughout. The numbers obtained for the width of the green slit are given in Table II.

The range between a noticeable excess and defect of green is for the unfatigued eye 4·5, and for the fatigued eye 16·2, and a match correct for the unfatigued eye is correct for the fatigued eye.

If the sensation curves are the same for a given observer as for the normal, except that one of them is shifted along the spectrum, quite a different result will be obtained. Thus suppose that the green-sensation curve is shifted towards the red end of the spectrum by an amount equal to

Table II.

Character of match.	Width of green slit.	
	Unfatigued.	Fatigued.
Correct	22·7	23·5
Too little green	20·5	11·0
Too much green............	25·0	27·2

2 S.S.N. and occupies the position shown by the dotted curves in figs. 1 and 2. The sensations at the points *a* and *b* for such a person are as follows:—

Table III.

Position of slit.	Sensations.		
	Red.	Green.	Blue.
a	67·9	79·2	1·6
b	1·4	0	67·7
Sums	69·3	79·2	69·3

The sums of the blue and red sensations are still equal but the sum of the green sensation ordinates is greater, and hence the mixed colour will not match the white but will appear to such a person too green. If, however, the yellow slit is moved towards the red to *c*, fig. 2 (S.S.N. 49·8, 5860 Å.U.) and the width of the violet slit is made 2·72 times that of the yellow slit we get

Table IV.

Position of slit.	Sensations.		
	Red.	Green.	Blue.
c	71·8	73·5	0·5
b	1·7	0	73·0
Sums	73·5	73·5	73·5

The three sums are now equal and hence the mixed colour will match the white to such an observer, although it will appear orange to normal vision.

Hence, if an observer does not agree with the normal when violet and yellow are matched to form white but requires that the yellow slit be moved towards the red to form a match, we conclude that his green-sensation curve is displaced towards the red and *vice versâ.* A movement of the red-sensation curve would produce a similar change but since we have not hitherto had an opportunity of finding such a case we shall in this paper only consider the effect of a shift of the green-sensation curve. It may, however, be pointed out that a shift of the red-sensation curve would be accompanied by an increase or decrease in the luminosity of the extreme red end of the spectrum according as the shift is away from or towards the green. As far as the shift of the green-sensation curve is concerned we have hitherto only met with displacements towards the red end of the spectrum.

In the case of a shift of the green-sensation towards the red amounting to 2 S.S.N. as indicated by the dotted curves in figs. 1 and 2 we should expect the following effects to be produced:—

1. The part of the spectrum which to the normal appears yellow will appear greenish, for owing to the displacement the green sensation excited will be greater than in the normal. In the same way what appears orange to the normal will appear yellow, and so on.

2. If we place three slits in the spectrum, one at the place of the red lithium line, *d*, fig. 2, another at the *b* magnesium line *e*, fig. 2, and the third in the violet at *b*, fig. 2, and by varying the width of the three slits produce a mixture which to the normal appears to match the white, this match will not appear correct to the observer with the green shift (whom, for short, we may designate by O., the normal being indicated by N.). To O. the match will be imperfect, for the green sensation he receives from the light passing through the green slit at *e* will not be as great as it is to N. By opening the green slit we can, however, obtain a match which is correct for O., but his match will appear green to N., and he will never agree that the normal match is correct.

If now we move the green slit to *f*, fig. 2, where the normal green-sensation curve cuts the displaced curve we shall find that a match which is correct for N. is also correct for O., and that either can detect a small departure from this setting.*

3. The above is one arrangement of the three slits such that O. and N. make the same match. Another such position is obtained if the red slit is moved to *g*, fig. 2 (S.S.N. 52·4, 6000 Å.U.). The light which now comes through the red slit excites green sensation in the case of both N. and O., but

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* We have neglected any small variation in the amount of violet which may be necessary owing to small differences of macular pigmentation.

to a greater extent in the case of the latter. Since the red and blue sensations are the same for both it will be sufficient to consider the equality of the red and green in the two cases. If the width of the red slit is 0·62 times that of the green we get the following values of the sensations on the equal area scales:—

Table V.

Position of slit.	Sensations.			
	N.		O.	
	Red.	Green.	Red.	Green.
e	21·1	48·5	21·1	34·5
g	43·8	16·4	43·8	30·4
Sums	64·9	64·9	64·9	64·9

where the sums are the same in the two cases and hence the mixture appears white to both N. and O. Thus if the red and green slits are kept in a constant position and the red slit is gradually moved up towards the green the matches made by O. appear to N. at first too green, but the excess of green gradually decreases till the red slit is at S.S.N. 52·4. If the red slit is moved further towards the green the mixture which appears correct to O. will then appear too red to N.

4. Owing to the displacement of the green-sensation curve O.'s *luminosity* curve will be higher than the normal on the red side of the point where the normal and displaced green-sensation luminosity curves cut and lower on the green side of this point, for the ordinates of the luminosity curve are the sums of the ordinates of the three luminosity sensation curves. The resulting luminosity curve for a displacement of 2 S.S.N. towards the red is shown in fig. 1 by the dotted curve, the corresponding normal curve being given by the thick continuous line.

Up to quite recently those observers who gave indications of a shift of the sensation curves have not been able to devote the time necessary for a full investigation. We have, however, been fortunate enough to have in the Senior Physics Class at the Royal College of Science this year a case of such a shift, and this gentleman (R.) has been good enough to devote the necessary time to carrying out a complete investigation of his colour sensations. He has proved to be a most accurate observer, and we can place complete reliance on his observations. He made a series of matches throughout the spectrum from which his sensation curves have been deduced in the manner described by one of us in a previous paper.* His red and practically his blue sensation curves are identical with those of the normal, but his green-sensation curve is markedly different. The numbers obtained for the green sensation are shown by the crosses in fig. 3. It will be observed that R.'s green-sensation curve is similar in shape to the normal, which is shown by the continuous line on the figure, but that it is displaced by about 2 S.S.N. towards the red end of the spectrum. Thus to him the maximum for the electric arc light occurs at wave-length 5690 Å.U. in place of at 5575 Å.U., which is that of the normal.

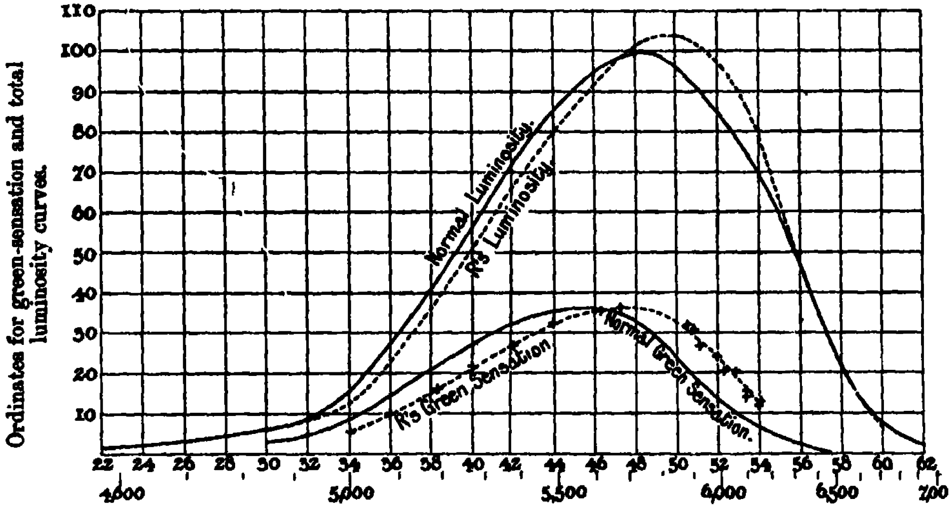

FIG. 3.—Scale of prismatic spectrum (S.S.N.), showing wave-lengths.

When white is matched by mixing light which passes three slits placed at the points *d*, *e*, and *b*, fig. 2 (6705, 5190, 4235 Å.U.), R. requires very much more green than the normal, as is shown by the first line in Table VI. If, however, the red slit is moved towards the yellow, the green and violet slits remaining fixed in position, the excess of green required by R. got less and less, till finally a position for the red slit was found where the mixture matched white both to R. and to the normal. If the red slit is moved further towards the yellow R. required less green than the normal, so that his mixture looked slightly red to the normal. The above changes indicated that in the case of R. we had to deal with a shift of the green-sensation curve. The changes in the slit widths required to match white both by R. and by a normal (W. W.) are shown in Table VI. The positions of the green and violet slits were kept constant, as was also the width of the green slit, the match being obtained by varying the widths of the red and violet slits and the brightness of the comparison white. With the red slit at 52·5 the match made by either was correct for the other.

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* 'Phil. Trans.,' 1905, A, vol. 205, p. 333.

Table VI.

Position of "red" slit.		Slit widths.					
		R.			W. W.		
S.S.N.	Å.U.	Red.	Green.	Violet.	Red.	Green.	Violet.
59·8	6710	28·3	17·2	26·0	62·5	17·2	26·0
57·1	6450	8·5	17·2	26·0	16·5	17·2	26·0
54·5	6200	7·2	17·2	26·0	8·6	17·2	26·0
53·0	6080	9·2	17·2	33·0	9·2	17·2	33·0
52·5	6040	10·4	17·2	33·0	9·5	17·2	33·0
52·0	6000	14·8	17·2	45·0	10·0	17·2	45·0

When matching D-light with a mixture of red and green light, if the red is at the red lithium line, R. required considerably more green than did the normal. If, however, the red slit were moved towards the yellow, just as in the case of the white matches, the excess of green gradually decreased, though, owing to the fact that the D-light in the case of R. excites the green sensation more strongly than the normal, we did not get the marked change in the appearance of R.'s match to the normal which has been referred to in the case of the white match. For this reason the white match is preferable to the Rayleigh match for bringing out the characteristic changes when the position of the red slit is altered. Another advantage of the white match is that the yellow produced by mixing green and red to match the D-light is less saturated than the D-light itself, and this causes considerable difficulty with some observers when making the match.

When matching white by a mixture of violet light (9·5 S.S.N., 4235 Å.U.) and yellow light the following results were obtained:—

	W. W.	R.
Position of yellow slit...	48·9 S.S.N. or 5780 Å.U.	50·0 S.S.N, or 5860 Å.U.

showing that the complementary to the violet is in the case of R. displaced towards the red, as has been shown on p. 237, we should obtain if the green-sensation curve was shifted towards the red end of the spectrum.

Again it was found that if the red and violet slits were in the standard positions *d* and *b*, fig. 2, a position for the green slit, *f*, fig. 2, could be found such that the mixed light matched white both for R. and for N.

The luminosity curve obtained by R., using the equality of brightness method, is given by the upper dotted curve in fig. 3, the continuous line being the normal curve. In fig. 4 are given the points corresponding to four sets of luminosity measurements made by the flicker method, the crosses giving the values obtained by R. and the circles those obtained by one of the authors (W. W.). It will be observed that R.'s luminosity curve agrees with what it ought to be if his green-sensation curve is displaced towards the green by about 2 S.S.N., such a calculated curve being given in fig. 1. Attention may be drawn to the fact that R.'s luminosity curve does not agree with the normal at S.S.N. 48·6, as it would if R.'s abnormality were due to a deficiency of either the red or green sensations as has been shown in a recent paper by one of us.*

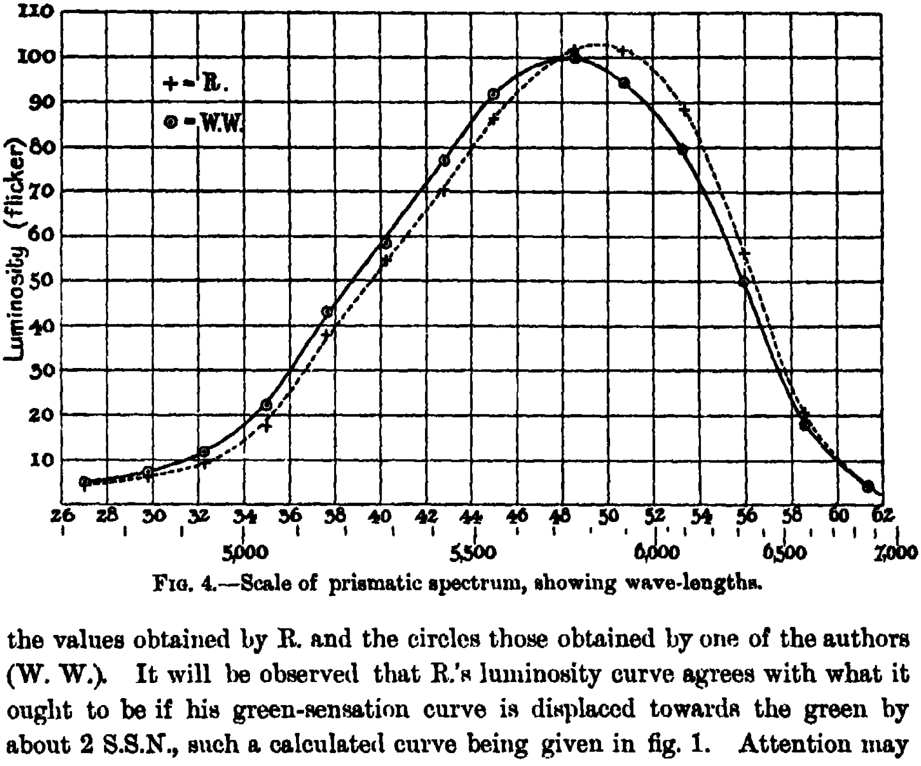

Fig. 4.—Scale of prismatic spectrum, showing wave-lengths.

It will thus be seen that the results obtained by R. agree in all respects with what we should expect if there is a shift of the green-sensation curve and which are given on p. 237, so that they form a strong support not only of the green-sensation curve obtained by R. but also of the normal curves published by one of the authors. Further, it is difficult to see how the various matches made by R., which are simply and consistently explained on the trichromatic theory, can be explained on any of the other commonly held theories of colour vision.

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* 'Roy. Soc. Proc.,' 1913, A, vol. 88, p. 404.

It is of practical importance to consider what effect a shift of the green-sensation curve such as that exhibited by R. will have on the power of discriminating colours, particularly those colours which are used as signals at sea and on railways. As has been mentioned, one effect of the displacement of the green-sensation curve is that the part of the spectrum which to the normal appears yellow, to such persons appears green or greenish. Thus R. places the change from green to yellow in the spectrum at 49·9 S.S.N. or 5810 Å.U. while to a normal (W. W.) this point appeared to be at 48·8 S.S.N. or 5780 Å.U. One effect of this difference is that a light, such as that given by a paraffin lamp, which to the normal appears decidedly yellow appears to a person with the shift of a greenish hue and in fact R. often calls such a light green.

Another effect of the displacement is that the perception of a green light when diluted with white light is very much more difficult than for the normal. The reason for this effect is at once apparent from a consideration of the sensation curves. Consider a green at S.S.N. 36 (5090 Å.U.). At this point in the spectrum the *red* and *blue* sensation curves for N. on the equal area scales intersect. Hence we may regard the effect produced by light of this wave-length as an amount of green sensation (represented by the difference between the ordinate of the green-sensation curve and the ordinate of either the red or the blue-sensation curves) diluted by white light (this white light corresponding to the equal amounts of red, green, and blue sensation excited). It will be observed that the amount of the *diluting white* is the same for the normal and the person with the displaced green curve; but to O. the amount of *residual green* sensation is less than half that of the normal. In other words the green perceived by R when light of this wave-length enters his eye is very much more diluted than it is to a person having normal colour vision. As a certain amount of dilution with white light will obliterate the perception of green in the coloured ray, it follows that to O. the amount of white light which will obliterate it is considerably less for O. than it is for a normal vision. This effect is clearly indicated by some measurements made by R. that are shown in fig. 5. The experiment consisted in determining the amount of any given coloured light which could be added to a given amount of white light so that in the resulting mixture the colour was only just recognisable. The ordinates in fig. 5 give the luminosity of the coloured light expressed as a percentage of the luminosity of the mixture, the crosses being the values obtained by R. and the circles those obtained by W. W. It will be observed that in the red the two agree as they also do in the blue. In the green, however, R. requires more than twice as much green light to be mixed with the white than does a person having normal colour vision.

To see whether the above given explanation is adequate to explain the effect observed in the case of R. we may calculate the proportion the residual green sensation bears to the total white, that is the added white plus the white due to the equal stimulation of the three sensations for the mixture of green at S.S.N. 35. The results are given in the following table:—

	Luminosity of colour when just perceptible (white = 100).	This colour consists of—		Total white.	Ratio of residual colour to total white.
		White.	Residual colour.		
R.	27·7	24·1	3·6	124·1	0·029
W. W.	9·9	6·6	3·3	106·6	0·031

It will be observed that the ratio of colour to white when the colour is just observable, when allowance is made for the want of saturation of the colour sensation is the same for R. as for the normal.

Another effect produced by this want of saturation is observed if the minimum brightness is determined at which a coloured light can be distinguished from a white light of the same intensity placed alongside, in other words, when the chromatic threshold is determined. In fig. 6 are given the illuminations on a screen (3·2 × 1·6 cm.) placed at a distance of 66 cm. from the eye when the coloured light looks indistinguishable from a similar patch of white light alongside. In the red and the blue R. and W. W. agree, but in the green there is a marked difference, R.'s threshold for colour being markedly higher than the normal.

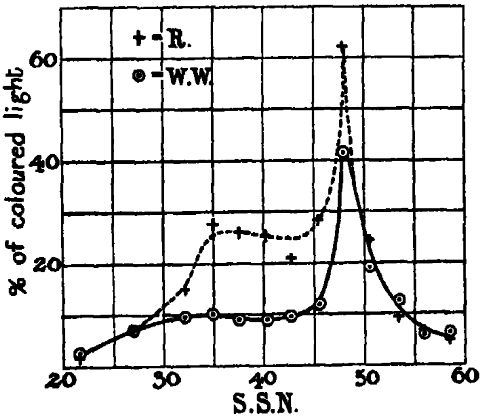

Fig. 5.

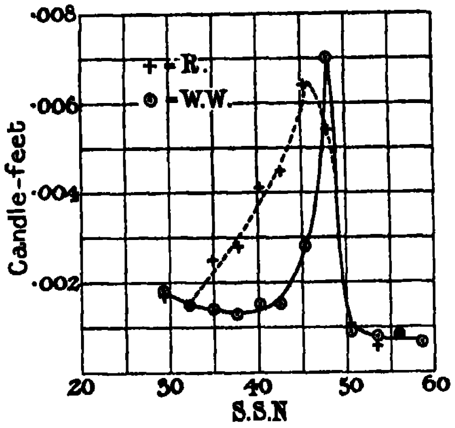

Fig. 6.

The above results both as to the effect of dilution with white and as to the chromatic threshold are of great practical importance, for they both affect the power of an observer to identify green lights such as those used at sea. These lights are never *pure* spectral lights, though they are spectral colours diluted with white. Thus the Board of Trade standard light-green light can be matched by a mixture of spectral green at S.S.N. 37·4 or 5115 Å.U., with an equal amount of white (arc light). Further, if the size of the image of the coloured patch on the retina is diminished, it must be remembered that the amount of white required to extinguish a spectral colour is very much reduced.

The increased want of saturation of the green produced by a displacement of the green-sensation curve towards the red is clearly brought out by the curves given in fig. 7. In this figure the spectrum is represented in terms of sensations on a triangular Newton's colour diagram. The corners of the triangle represent the red, green and blue sensations, the scale adopted being the equal area scale used in fig. 2, so that the centre W of the triangle represents white. The amount of either of the sensations corresponding to

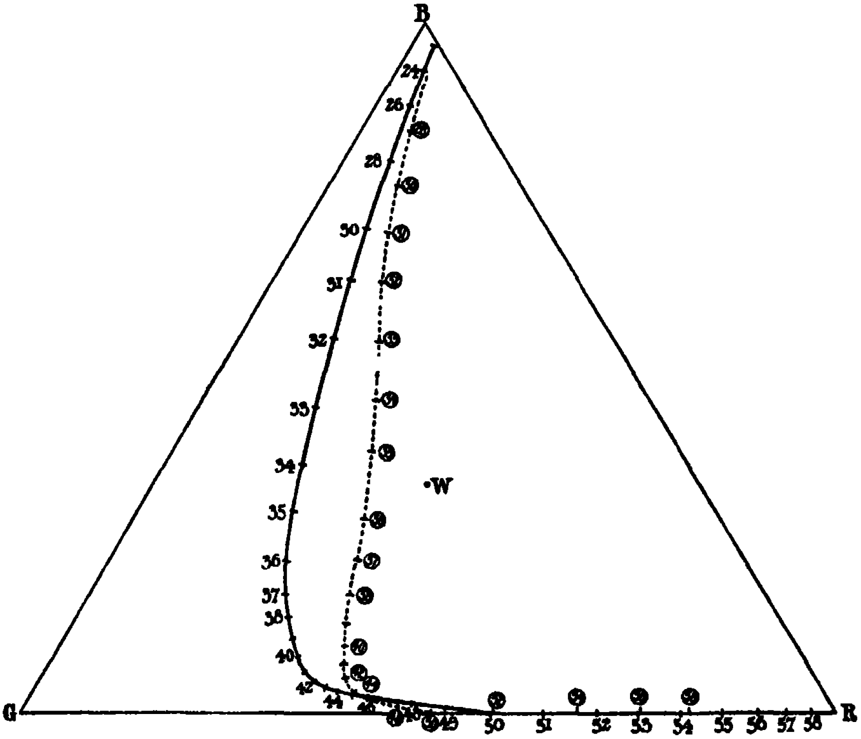

Fig. 7.—Newton's colour diagram of the arc-light spectrum.
The three colour sensations which make white light being shown as of equal value.

any point within the triangle is inversely proportional to the distance of this point from the corner corresponding to that sensation. The spectrum, as it appears to the normal eye, is represented by the continuous line, the numbers written alongside the line representing the different parts of the spectrum expressed in S.S.N. The dotted line gives the spectrum as it appears to a person who has the green-sensation curve displaced by 2 S.S.N. towards the red. Even to the normal eye the green part of the spectrum corresponds to a green sensation diluted by much white, for the curve representing the spectrum passes about half-way between the green-sensation corner and the white point W. In the case of the green-sensation shift the curve passes much nearer the white point W, indicating that the colour seen is less saturated than it is to the normal eye. If the green-sensation curve were shifted by 3·6 S.S.N. towards the red, the green-sensation curve on the equal area scale (fig. 2) would pass through the point where the red and blue sensation curves intersect, and hence light of the wave-length (5090 Å.U.) corresponding to this point would produce the sensation of white to such a person. In other words, there would be a neutral point in his spectrum. In such a case the curve representing the spectrum on the Newton diagram would pass through the point W.

As a result of our study of the case of R., as well as of some more isolated observations made on others, we consider that it is extremely probable that the particular class of colour abnormality which was first investigated by Lord Rayleigh by means of his instrument for matching D-light by a mixture of red and green light, and which is generally referred to as anomalous trichromatism, is due to a shift of the sensation curves, and that green anomalous trichromates are persons who have the green-sensation curve displaced towards the red end of the spectrum. It must, however, be remembered that abnormal matches may be obtained by persons who in place of a shift have a reduced sensation for red or green. The two classes are, however, distinguished, as has been pointed out earlier, by the fact that in the case of a deficient sensation the accuracy with which matches can be made is less than in the case of either the normal eye or one in which one of the sensation curves is shifted.

In conclusion, the authors would like to express their obligation to Mr. R., to whose careful measurements they are indebted for many of the results which are embodied in this communication.

The Reflection of X-rays by Crystals. (II.)

By W. H. Bragg, M.A., F.R.S., Cavendish Professor of Physics in the
University of Leeds.

(Received June 21,—Read June 26, 1913.

This note is a supplement to a paper on the reflection of X-rays by crystals which has been recently communicated to the Royal Society.[*] It is there shown that the wave-length of a homogeneous beam of X-rays can be found accurately in terms of the spacing of the elements of a crystal. There has been some doubt as to the actual arrangement of the atoms in the crystal and in consequence it was not possible in the paper quoted to draw any final conclusions as to wave-length values. From the work now described by W. L. Bragg it appears that the reflection phenomena lead to a more definite knowledge of crystal structure, and we may now complete various quantitative determinations.

The elementary volume in rock-salt is a cube with 1 atom of sodium at each of four corners and 1 atom of chlorine at each of the other four. In other words the number of elementary volumes in any space of measurable dimensions is equal to the number of atoms in that space.

The number of molecules in 1 c.c. of NaCl is

$$2{\cdot}15/58{\cdot}5 \times 1{\cdot}64 \times 10^{-24} = 2{\cdot}24 \times 10^{22}.$$

(The weight of the H atom is taken to be $1{\cdot}64 \times 10^{-24}$.)

The number of atoms is twice as great and the elementary cube volume is therefore $1/4{\cdot}48 \times 10^{22} = 2{\cdot}23 \times 10^{-23}$. The edge of the cube is $2{\cdot}81 \times 10^{-8}$; this is the distance between consecutive reflecting planes parallel to (100).

The principal bundle of homogeneous X-rays from a platinum anticathode is stated in the paper quoted to be reflected at the (100) face of rock-salt at a glancing angle of 11·55°. Recent observations with better apparatus show that this bundle is really double, consisting of two separate sets whose wave-lengths differ from each other by a little less than 2 per cent. of either; they also show that the first estimate was a little too high. For the purpose of the present argument it is sufficiently accurate to ignore the division and assume the angle to be 11·3°. This gives a wave-length

$$(2\,d \sin\theta) = 2 \times 2{\cdot}81 \times 10^{-8} \times 0{\cdot}196 = 1{\cdot}10 \times 10^{-8}.$$

The wave-lengths of other homogeneous rays can then be found easily as soon as their angles of reflection are known.

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[*] W. H. Bragg and W. L. Bragg, these 'Proceedings,' A, vol. 88, p. 428.

A bulb having a nickel anticathode gives one weak beam of homogeneous rays reflected at a glancing angle of 17·2°; the corresponding wave-length is $1·66 \times 10^{-8}$. A tungsten anticathode gives a weak beam at an angle of 12·9° and the wave-length is therefore $1·25 \times 10^{-8}$. An iridium anticathode gives a more complicated spectrum which is not yet completely analysed.

On the basis of existing theories certain numerical relations might be expected to subsist between these quantities, and it is interesting to see how closely they are fulfilled.

In the first place the "quantum" energy for a wave-length $1·10 \times 10^{-8}$ is $6·55 \times 10^{-27} \times 3 \times 10^{10}/1·10 \times 10^{-8} = 1·78 \times 10^{-8}$ ergs. This should be the value of the energy of the cathode ray which can excite this particular X-ray, as well as of the cathode ray which it can excite. The quality of the X-ray can be expressed in terms of its mass-absorption coefficient in aluminium. The estimate of this quantity given in the first paper quoted was too low; the influence of the scattered radiation was not effectively removed. By taking the mean of the radiation on either side of the B peak and subtracting this from the radiation at the peak itself with and without an Al screen a value 23·7 is found. That the radiation is very homogeneous is ascertained in the usual way.

Now according to Barkla's experimental results, X-rays of this quality are such as are given in the K series by a radiator of atomic weight 74 and in the L series by a radiator of atomic weight 198. The atomic weight of platinum is 195, and this can hardly be a coincidence. It may be calculated from Whiddington's results* that the energy of the cathode ray required to excite the X-ray of the K series in an atom of weight 74 is about $2·14 \times 10^{-8}$ ergs, which is in very satisfactory agreement with the "quantum" energy calculated above.

From the foregoing it seems reasonable to take the radiation of the B peak as equivalent to the characteristic radiations of an atom of atomic weight 74 (or perhaps 72·5, the equivalent of platinum in the K series), while the experiment with the nickel anticathode may be taken to show that the wave-length $1·66 \times 10^{-8}$ belongs to nickel (at. wt. 59) and in the same way that of $1·25 \times 10^{-8}$ to tungsten in the L series or its equivalent (at. wt. 67) in the K series. Now the quantum energies should be proportional to the frequencies and at the same time according to Whiddington to the squares of the atomic weight. The squares of 59, 67, and 74 (or 72·5) are in the ratio 100 : 130 : 157 or 150, while experiment shows that the frequencies are in the ratio 1/1·66 : 1/1·25 : 1/1·10, or 100 : 132 : 151. The frequency is therefore very nearly proportional to the quantum energy.

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* 'Proc. Camb. Phil. Soc.,' vol. 16, p. 150.

Lastly, though the absorption coefficient of the tungsten peak has not yet been satisfactorily measured, it may be doubtless supposed to be a little less than that of the A peak of platinum, since its wave-length is slightly less. A recent measurement of the latter quantity gives the value 35·5 and the absorption coefficient of the characteristic radiation of tungsten is given by Barkla as 33.

The Structure of Some Crystals as Indicated by their Diffraction of X-rays.

By W. L. Bragg, B.A.

(Communicated by Prof. W. H. Bragg, F.R.S. Received June 21,—Read June 26, 1913.)

[Plate 10.]

A new method of investigating the structure of a crystal has been afforded by the work of Laue* and his collaborators on the diffraction of X-rays by crystals. The phenomena which they were the first to investigate, and which have since been observed by many others, lend themselves readily to the explanation proposed by Laue, who supposed that electromagnetic waves of very short wave-lengths were diffracted by a set of small obstacles arranged on a regular point system in space. In analysing the interference pattern obtained with a zincblende crystal, Laue, in his original memoir, came to the conclusion that the primary radiation possessed a spectrum consisting of narrow bands, in fact, that it was composed of a series of six or seven approximately homogeneous wave trains.

In a recent paper† I tried to show that the need for assuming this complexity was avoided by the adoption of a point system for the cubic crystal of zincblende which differed from the system considered by Laue. I supposed the diffracting centres to be arranged in a simple cubic space lattice, the element of the pattern being a cube with a point at each corner, and one at the centre of each cube face. A simpler conception of the radiation then became possible. It might be looked on as continuous over a wide range of wave-lengths, or as a series of independent pulses, and there was no longer any need to assume the existence of lines or narrow bands in its spectrum.

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* W. Friedrich, P. Knipping, and M. Laue, 'Münch. Ber.,' June, 1912.

† 'Camb. Phil. Soc. Proc.,' November, 1912.

It is the object of this paper to extend the analysis used in the case of the zincblende to some other crystals, particularly those of the simple alkaline halides.

In treating the diffraction of waves by a space point system such as a crystal, that case is the most simple in which the diffraction is caused by a series of points arranged in a space lattice, of one of the 14 Bravais types. Here every point is identical with every other point of the arrangement, and it is always possible to find an element of the pattern consisting of a parallelepiped with a point at each corner: there will then be as many parallelepipeds as atoms in any space. The points can be referred to three axes parallel to the edges of the parallelepiped, and if one of the points is taken as the origin the co-ordinates of the others may be written

$$x = \pm pa, \qquad y = \pm qb, \qquad z = \pm rc,$$

where p, q, r are any integers, and a, b, c are equal to the sides of the parallelepiped, and therefore proportional to the axial ratios of the space lattice. When the axes are chosen in this way the co-ordinates of the points and the equations of the planes passing through given selections of points are expressed in the simplest manner possible.

Let a series of pulses fall on this space lattice, the direction of propagation having a given relation to the axes of the system. As any one pulse passes over each point, a diffracted wavelet spreads from it, and it will be shown that the wavelets from all the points due to one incident pulse will combine in certain directions to form trains of waves, which give rise to the patterns of spots appearing in Laue's diffraction patterns. This may be done in the following way:—

If the axial ratios of the space lattice be denoted by a, b, c, any plane which makes intercepts pa, qb, rc, on the axis (p, q, r being any integers) is parallel to a whole set of planes on which the points of the system may be considered as arranged. It is such planes as these which form the faces of a crystal. When a pulse falls on a set of points on a plane the wavelets from the points combine to build up a wave front which will appear to be regularly reflected from the plane. As there are a series of planes regularly spaced one behind the other, a single pulse falling on them gives rise to a reflected wave train.

When therefore a narrow pencil of X-rays falls on a section of a crystal, part of its energy is transmitted undeviated, but there is also a part which is reflected on the crystal planes existing potentially in the body of the crystal. It is the series of narrow beams arising by reflection in this way which gives rise to the pattern of spots appearing in the photograph.

There can be assigned to each set of parallel planes integral indices (h, k, l), as when naming the faces of a crystal, and a spot can be classified as being reflected in the (h, k, l) set of planes. Here the integers h, k, l, are reciprocal to the intercepts which a parallel plane makes on the axis of reference. They are Millerian indices, the equation of the plane being

$$h\frac{x}{a}+k\frac{y}{b}+l\frac{z}{c} = \text{an integer.}$$

They may be considered as the parameters of each spot of the pattern, and are exactly equivalent to the parameters (h_1, h_2, h_3) employed by Laue in his original treatment of the subject. Laue defines his parameters by saying that the diffracted wavelet from a point at the origin of co-ordinates lags h_1, h_2, h_3, wave-lengths in the directions under consideration behind the wavelets proceeding from its neighbours along the x, y, z axes respectively. Thus the wavelets from all atoms in the plane

$$h_1\frac{x}{a}+h_2\frac{y}{b}+h_3\frac{z}{c} = 0$$

are in phase with that from the origin, and, in general, the wavelets from all points in the plane

$$h_1\frac{x}{a}+h_2\frac{y}{b}+h_3\frac{z}{c} = \text{an integer}$$

are in the same phase. We are led back to the same conclusion as before, that the direction of the diffracted wave front is one in which the primary beam is reflected by planes whose Millerian indices are (h_1, h_2, h_3). But, as will appear presently, it is important to bear in mind the fact that crystal structure alone fixes the exact position of the interference maxima, quite independently of the existence of homogeneous components of definite wave-length in the incident rays, and therefore a method of treatment has been adopted in which all reference to the wave-length has been avoided.

It is possible for a spot to appear in a position corresponding to reflection in any set of planes having integral indices (h, k, l). In an actual pattern obtained by allowing the diffracted X-rays to fall on a photographic plate, since there is not an infinite number of spots, only a selection of the planes can be operative. The spots forming the pattern are of very different intensities, and one can never say that spots are entirely absent but merely that in certain cases the rays are too weak to make an impression. It would seem, however, that by classification of the planes which reflect the principal spots of the pattern a clue can be got to the true point system arrangement of the diffracting centres. The point system which affords the most simple interpretation of the pattern is that which ought to be taken as representing the crystal structure.

When a photograph has been taken with a crystal an analysis is necessary in order to assign to each spot of the pattern obtained the correct parameters *h*, *k*, *l*, the Millerian indices of the face from which the spot is reflected. Having decided on the axes of reference of the crystal, the following method will be found to apply whatever their inclinations to each other and axial ratios may be.

The more important planes of the system are those densely packed with points, and from this fact it follows that these planes contain rows along which the points are closely packed. These are the important "point-rows" of the crystal, and each of these point-rows will have a set of important planes parallel to it. The three axes themselves are the most obvious examples of these point-rows. The "zone axis" of planes belonging to a common zone is also such a direction. There is a convenient relation between the points which are reflected in the planes belonging to any one zone. The reflected beam always lies on a circular cone with apex at the crystal section, the zone axis as axis, and the direction of the primary beam as one generator. This cone cuts the photographic plate in an ellipse passing through the central point of the pattern, and all spots reflected in planes of the zone lie on it. The arrangement of the spots on ellipses is very obvious in an interference pattern (see fig. 11), and the ellipses can immediately be drawn. A little calculation shows to which zone axis each ellipse must be assigned, and, by marking a given spot as lying on the intersection of two ellipses, the calculation of the indices h, k, l, of that spot is made possible. For each zone of planes we have the relation $h\mathrm{U}+k\mathrm{V}+l\mathrm{W}=0$ where (U, V, W) is the zone symbol; that is to say, the set of direction ratios of the zone axis.

When representing diagrammatically an interference pattern it is very inconvenient to draw the ellipses at the intersections of which the spots of the pattern lie. It is simpler to employ an extension of the usual stereographic projection of crystallography. Reference to fig. 1 will make this clear. Let the section of crystal be situated at C, the centre of the sphere represented in the figure by the circle ABP, and let the direction of the incident rays be from P to C. The rays which traverse the crystal undeviated fall on the photographic plate AD at A. Let CZ represent the direction of a zone axis. The beams reflected in planes of this zone lie on a circular cone with vertex at C, of which CZ is the axis, and CA, CB are two generators.

This cone cuts the sphere in a circle of which AB is a diameter, and by the well known property of the stereographic projection, the projection of this circle on the plane AD from the pole P is also a circle. The centre of this circle is at Z, since AZ = ZS′, Z being the point where the zone axis cuts the photographic plate.

Let the pattern of spots be supposed to be made by the diffracted beams on the sphere ABP, and this pattern projected on the plane AD from the pole P. Spots corresponding to reflection in planes of a zone now lie on a circle, having its centre at the point where the zone axis cuts the plate AD. The spot at S made by the reflected beam CB becomes a spot at S′ of the transformed pattern. The distortion of the pattern of spots by the transformation is very small except in the regions distant from the centre, and circles are much easier to draw than ellipses. This has been done in all the diagrams given in this paper. In constructing a diagram, a point is chosen as that in which the incident rays meet the photographic plate. This is A in the figure. Then the points such as Z, where the principal zone axes meet the plate, are found by a calculation, which is easy when the crystal is placed symmetrically to the pencil of X-rays. A circle is drawn with centre Z and radius ZA. This being done for each zone axis, the intersections of the circles give the stereographic projections of the reflected spots.

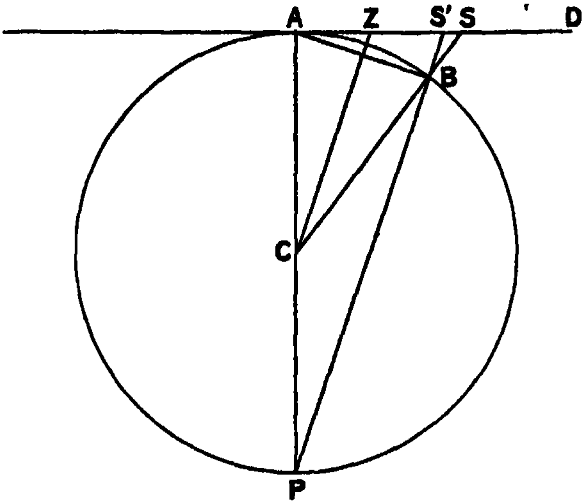

Fig. 1.

Let us take as an example of the application of this analysis the very simple case of potassium chloride. The diffraction pattern obtained when the X-rays fall normally on a plate cut parallel to the cube face (001) is reproduced in fig. 2, Plate 10, and its stereographic projection in fig. 3, which shows also the indices of the reflecting planes corresponding to the several points of the photograph.

Potassium chloride is cubic, and the indices given to the planes are those obtained when the edges of the cube are selected as axes of reference.

The circles correspond to zone axes for which

$$\left.\begin{matrix} U = 0, & V = \pm 1 \\ U = \pm 1 & V = 0 \end{matrix}\right\} W = 0, 1, 2, 3, 4, 5,$$

and their intersections give the spots reflected in all planes of the form $(h\,k\,1)$ where h and k have any of the values

$$0,\ \pm 1,\ \pm 2,\ \pm 3,\ \pm 4,\ \pm 5.$$

In the diagram of the KCl pattern the spots are represented by dots, the magnitude of each dot indicating the strength of the corresponding spot in the photograph. It will be seen how complete the pattern is, and how within a certain range each intersection is represented by a spot in the photograph.

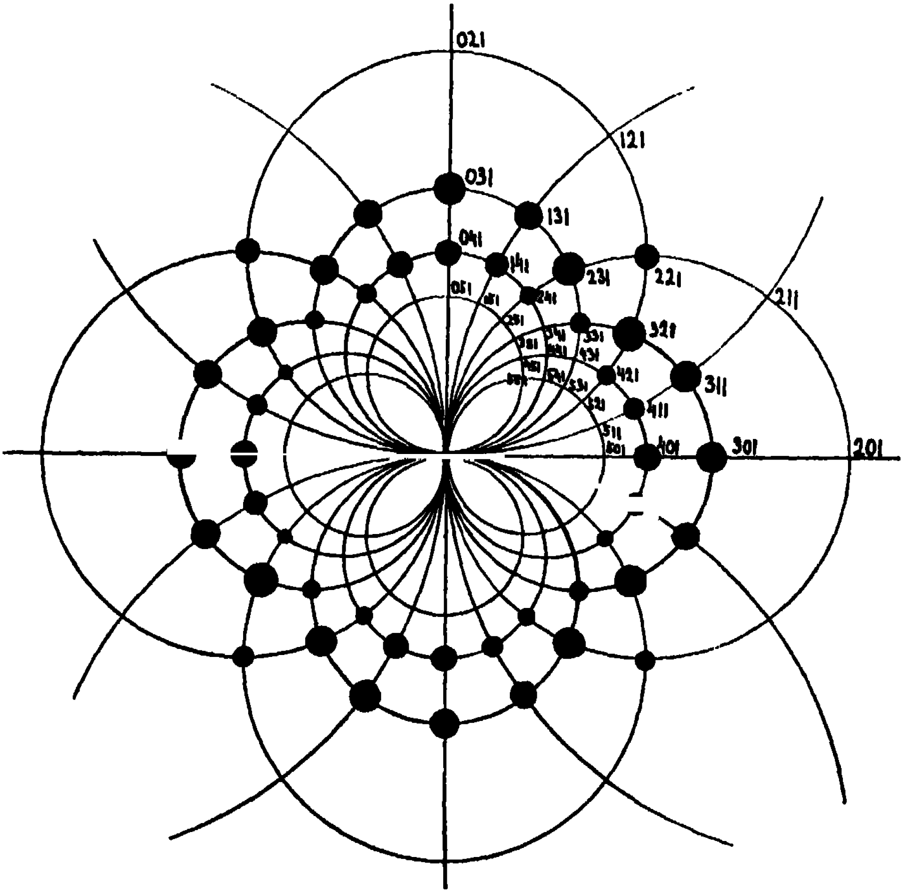

Fig. 3.—Potassium chloride.

This may be put in another way. Below is a table of values of h and k, l being equal to 1. In the square corresponding to given values of h and k

is placed a dot denoting the magnitude of the corresponding spot, the square being left empty if no spot is to be seen.

Table I.

KCl.

k ↓ h →	0	1	2	3	4	5
0				✳	✱	
1				✳	✱	
2			✳	✳	+	
3	✳	✳	✳	+		
4	✱	✱	+			
5						

This table contains a list of all the spots appearing in the photograph. It suggests that the diffraction is due to a simple cubic space lattice, for when the elementary parallelepiped is a cube and its edges are taken as axes the indices of the planes naturally take these simple forms.

For, let a series of planes be taken, for which two indices are constant and one varies, such as the series 031, 131, 231, 331, 431, etc. These planes will be arranged in this order for all their properties, such as reticular density, distance apart, and so forth, if, and only if, the indices are referred to axes parallel to the sides of the elementary parallelepiped. If this condition is satisfied, then all the properties of the planes vary in an orderly manner as one passes along the series. The power of reflecting the X-rays is a particular property of the planes, which is seen from the photograph to vary continuously for any such series as the one given above, therefore the diffracting system is a space lattice with axes at right angles, and a cube for its elementary parallelepiped.

It may be objected here, that it is conceivable that a complex structure, and a radiation consisting of homogeneous components, just happen in the case of potassium chloride to give a deceptively simple pattern. That this is not the case can be seen by displacing the crystal from its symmetrical position, and obtaining the distorted interference pattern. It is still as straightforward as before, though of course no longer symmetrical. Corresponding spots in the two patterns are now made by different wave-lengths, and it is obvious that there can be nothing of the nature of homogeneous components of the incident radiation. The contrast of this pattern with those characteristic of potassium bromide and iodide, of rock salt, and of zincblende, which will shortly be given, will tend to make this more clear.

All the most intense spots of the photograph are at about the same distance from the centre of the pattern. A circle can be drawn such that the spots which lie near to it are very intense, while those further away are weaker and those at great distances are too faint to appear. All ellipse intersections lying near this circle are represented by a spot. Those planes reflect most strongly for which the glancing angle lies between 12° and 20° and it is in seeking to explain this fact that it is necessary to consider the question of the "wave-length" of the diffracted rays. This we must now do.

When a pulse falls on a series of planes regularly spaced one behind the other, it is reflected as a wave train, and the waves making any one spot must be considered to be of the lengths given by

$$n\lambda = 2d \sin \theta,$$

where θ = glancing angle, d = distance between successive planes, and n is an integer 1, 2, 3, etc. An alternative way of regarding the phenomenon is to consider the incident radiations as compounded of homogeneous wave trains of all wave-lengths, with a characteristic distribution of energy in the spectrum, when the parallel planes must be considered as reflecting only that part of the spectrum for which the relation $n\lambda = 2d \sin \theta$ holds good. In the case of the cubic space lattice considered here, this relation reduces to

$$n\lambda = \frac{2a}{l} \sin^2 \theta,$$

where a is the distance between neighbouring points along the cubic axes, for a simple calculation shows that $d = a \sin \theta / l$. Since l is equal to unity for all the spots of the potassium chloride photograph, spots which have the same θ, and lie at the same distance from the centre of the pattern, correspond to the same wave-length. The ring of intense spots in the pattern indicates strong reflection of a certain part of the spectrum of the incident radiation. Either conditions are especially good[*] for reflecting this wave-length, or the incident rays have a large amount of their energy in this part of the spectrum.

It is interesting to compare the simple pattern of potassium chloride with those of potassium iodide, potassium bromide, fluorspar, and zincblende.

The stereographic projection of KBr (100) is given in fig. 4, that of KI being very similar. Both of these are like the patterns of zincblende and fluorspar, and are in marked contrast to that of KCl.

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[*] The most important condition in this connection is probably the thickness of the crystal section used. As will be shown later, the use of a thin crystal section favours the reflection of the longer wave-lengths, the corresponding spots coming out strongly, while the use of a thick section favours the reflection of the shorter.

It is evident that some factor has now entered which destroys the simplicity of the arrangement of spots characteristic of potassium chloride. Spots no longer appear at every intersection of the ellipses within a certain region, as in fig. 3. A tabulation of the intensities of the spots in the zincblende and potassium bromide patterns will make this clear. (See Tables II and III.)

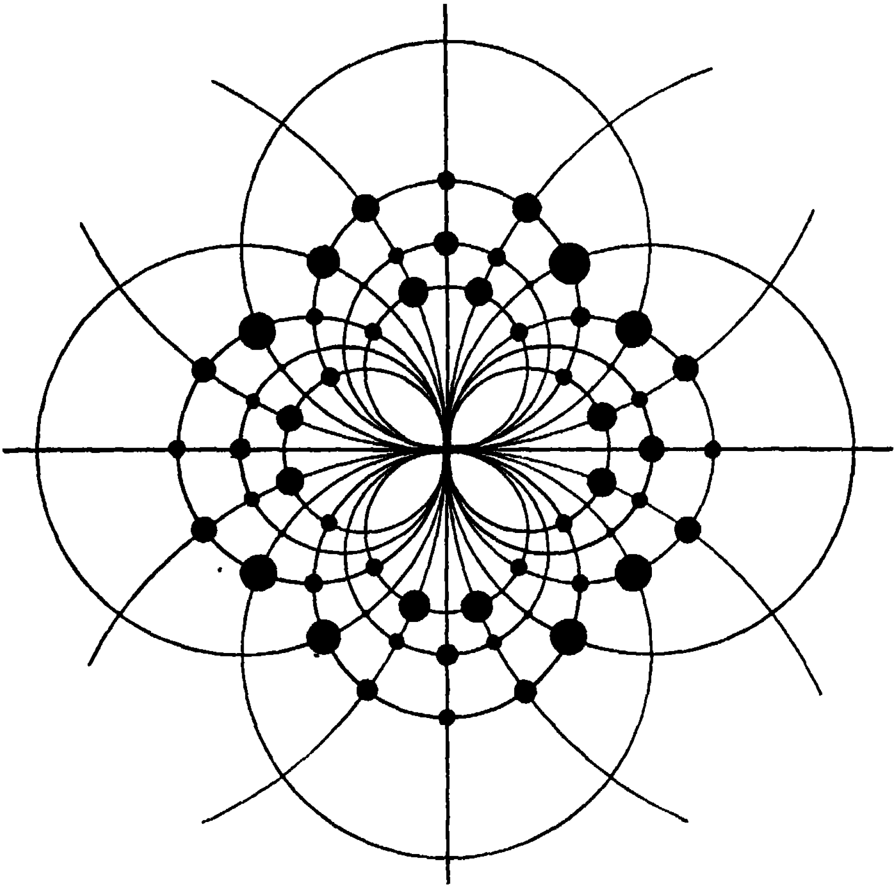

FIG. 4.—Potassium bromide.

There are also in the case of zincblende several spots for which a value 3 must be assigned to *l*, if *h* and *k* are to be integers, but not many. It was a consideration of Table II which led in a former paper* to the conclusion that the diffracting centres of the zincblende crystal are arranged on the face-centred cubic space lattice.

An examination of the planes in which reflection takes place shows that there is a differentiation between those whose indices are wholly odd and

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* 'Camb. Phil. Soc. Proc.,' November, 1912.

Table II.

Zn.S.

k ↓ h →	0	1	2	3	4	5	6	7
0				✚				
1			•	✚	✶	✳		+
2		•	•	✳	+			
3	✚	✚	✳	✚	+	✳		+
4		✶	+	+				
5		✳		✳		+		
6								
7		+		+				

Table III.

K.Br

k ↓ h →	0	1	2	3	4	5
0				+	✶	
1				✶	✚	✳
2				✳		
3	+	✶	✳	✚		✶
4	✶	✚				
5		✳		✶		
6						
7						

those which have one or more even indices. If those planes alone are considered which have odd indices, as in the following table, the scheme is as complete as it was for the spots of the KCl crystal.

Table IV.

Zn.S. (odd indices only)

k ↓ h →	1	3	5	7	9
1		+	✳	✚	
3	+	✶	✳	•	
5	✳	✳	+		
7	✚	•			
9					

Odd planes, ZnS.

Table V.

Zn.S. (even indices only)

k ↓ h →	0	1	2	3	4	5
0				✚		
1		▥	•	▥	✶	▥
2		•	✚	✳	•	
3	✚	▥	✳	▥	•	▥
4		✶	•	•		
5		▥		▥		▥

Even planes, ZnS.

The same is true for those with an even index* except that the intense spots are all further removed from the centre of the picture.

This difference can be explained without our being forced to assume that the diffracting system is anything more than a simple system of identical points. It is sufficient to suppose that the point system has points at the centres of the cube faces as well as at the cube corners. Let a cubic point system of the first kind be taken which has points at cube corners alone, and let points be introduced at the cube face centres in order to turn it into a point system of the so-called "third kind." (The "second kind" is the centred cube.) The spacing of the planes which have odd indices (h, k, l) is not altered by the introduction of the new points, for they all lie on the original planes and only increase their point density. On the other hand, in the case of planes having an even index, some of the new points lie halfway between the original planes, the distance between the successive planes of this type must now be halved, and so must therefore the wave-lengths of the reflected beams.

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* The spot 041 forms an exception, indeed evidence is not lacking that the assumption of diffraction by the face-centred space lattice does not completely account for the pattern. The reason for this will appear when the parts played by the atoms of two kinds in the diffraction are discussed.

The interpretation of the zincblende pattern is now simple. We have seen that the planes with odd indices only are a complete set. There are fewer spots corresponding to reflection in planes with an even index, for these planes are, relatively to the former, less closely packed, and of a more complex nature. Moreover, they are, at the same time, less widely separated, and therefore the intense spots with even indices are further from the centre; the angle of incidence must be increased in order to make these planes reflect that region of the spectrum which gives intense spots. By assuming the third cubic space lattice instead of the first, all the intense spots of the pattern again correspond to the same wave-length region.

The difference between the diffraction by the two cubic space lattices may be put in a much clearer way on analysis of the patterns of threefold symmetry, obtained when the incident rays fall normally on a plate cut perpendicular to a trigonal axis. If the points of the space lattices are considered from this aspect, they are special cases of the trigonal rhombohedral space lattice, one of the Bravais types.

The axes to which the spots ought to be referred are not the same for the two cubic lattices. When the points are at cube corners alone, the axes along which they are nearest neighbours are the cube edges, and the cube itself is the elementary parallelepiped. When there are also points at the centres of the cube faces, three semi-diagonals of cube faces meeting in a corner form three edges of the elementary parallelepiped. The angles between the axes are right angles in the first case, in the second they are 60°.

It will now be clear that when the stereographic diagram is constructed, giving the positions of the spots reflected from the simple planes of a trigonal rhombohedral space lattice, one such diagram will represent the patterns of all rhombohedral lattices, the alteration of the angle between the axes, *i.e.*, the rhombohedral angle, only causing an alteration of the scale of the diagram. The radius of the sphere used in the projection is, of course, supposed to be always the same.

Given the points where the three axes of the lattice meet the diagram, the corresponding points for the other zone axes can immediately be found and the whole diagram drawn. Such a diagram is shown in fig. 5, X, Y, Z, being these axial points, Now, our study of the patterns of fourfold symmetry given by potassium chloride and zincblende has shown that the axes of the lattice, which is from this aspect a special case of the rhombohedral lattice, make angles of 90° with each other in the first case, and of 60° in the second. Therefore it ought to be possible to refer the threefold patterns of potassium chloride and zincblende to the same trigonal lattice diagram, the scale being different, however, in the two cases. This conclusion is exactly confirmed by experiment. The pattern given by zincblende was published by Laue in his original memoir. The stereographic projections of the zincblende and potassium chloride patterns are given in figs. 6 and 7. The object of this comparison is to show that the spots of the KCl pattern fall naturally on

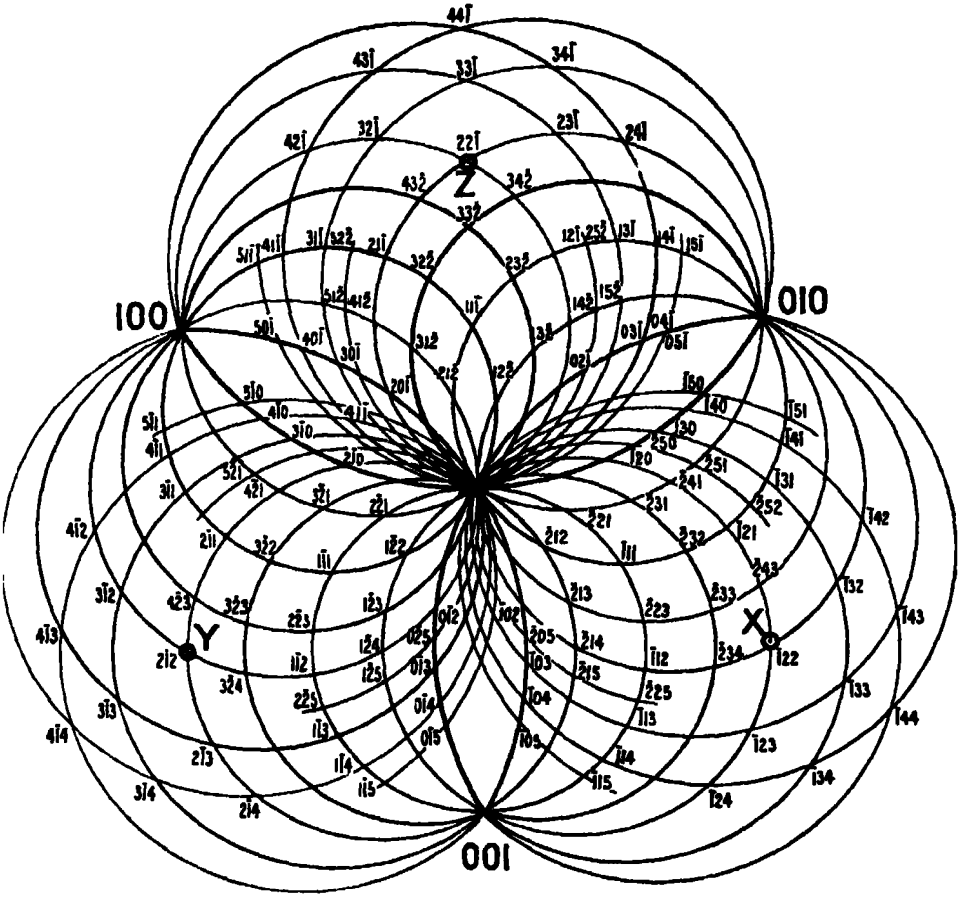

Fig. 5.

a diagram twice the size of that on which the spots of the ZnS pattern are arranged, the points where the axes making 90° with each other cut the plate, being just twice as far apart as for axes making 60° with each other.

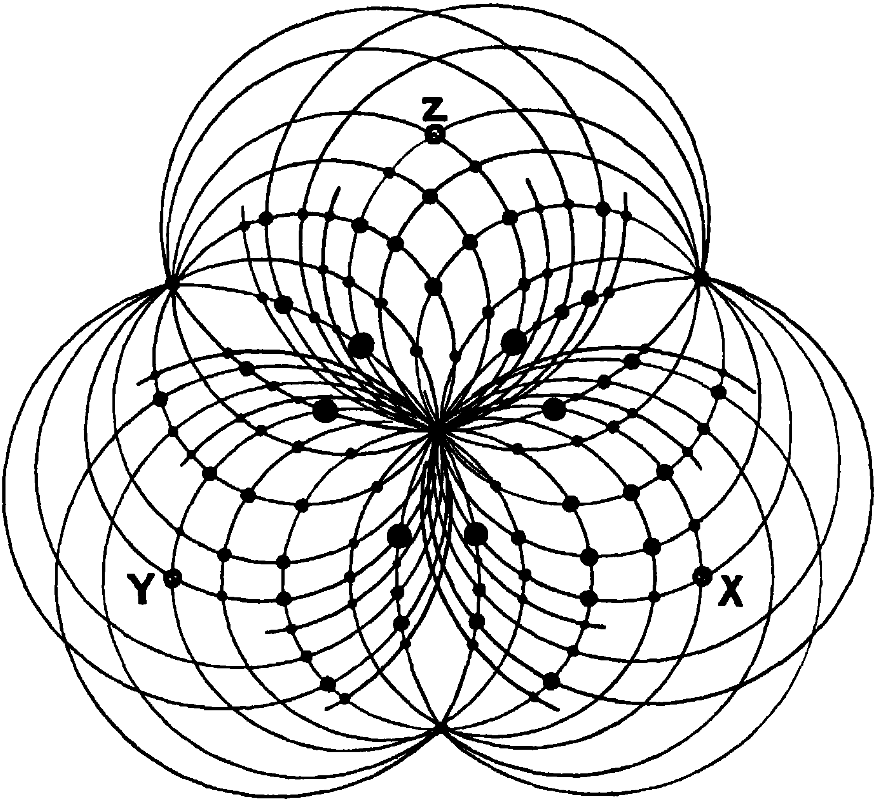

Fig. 6.—Zincblende.

The following table will illustrate the awkwardness of referring either pattern to the wrong diagram.

If the spots of the zincblende pattern are referred to the cubic axes, their indices become very much more complicated, and the pattern is no longer complete. The converse is true for the potassium chloride pattern, the indices in this case being simpler when referred to cubic axes. In Table VI a list of indices of the spots of each pattern is set down referred to (A) the cube edges, (B) the cube face diagonals, *i.e.*, three edges of the regular tetrahedron, as axes.

It will be seen that in the case of zincblende it is the B series, in the case of the potassium chloride the A series, which is simple, and which gives a complete series of indices over a certain range. I do not think there can be any doubt which space lattice is the right one in either case.

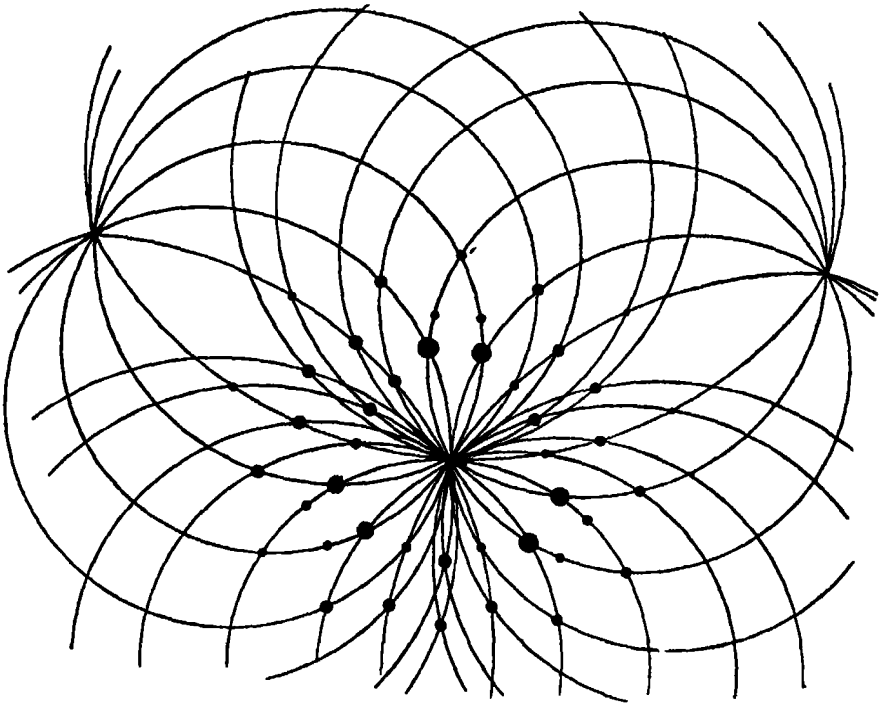

Fig. 7.—Potassium chloride.

Table VI.

Zincblende.				Potassium chloride.*	
A.	B.	A.	B.	A.	B.
$\bar{1}11$ $\bar{3}32$ $\bar{5}53$ $\bar{2}21$ $\bar{3}31$ $\bar{1}10$	010 $0\bar{5}1$ $0\bar{4}1$ $0\bar{3}1$ $0\bar{2}1$ $0\bar{1}1$	$\bar{1}11$ $\bar{3}75$ $\bar{1}32$ $\bar{1}53$ $\bar{1}95$ $0\bar{2}1$ 178 $1\bar{3}1$ $\bar{3}51$	100 $51\bar{1}$ $41\bar{1}$ $31\bar{1}$ $52\bar{2}$ $21\bar{1}$ $32\bar{2}$ $11\bar{1}$ $12\bar{2}$	$3\bar{1}\bar{1}$ $20\bar{1}$ $31\bar{2}$ $11\bar{1}$ $30\bar{2}$ $21\bar{2}$ $4\bar{1}\bar{1}$ $32\bar{3}$	$11\bar{1}$ $21\bar{1}$ $41\bar{1}$ 100 $31\bar{2}$ $30\bar{1}$ $33\bar{2}$ $50\bar{1}$

* The indices of the A series for the KCl pattern may not, at first sight, appear simpler than those for the B series. The B series, however, is curiously incomplete. For instance, $21\bar{1}$ and $41\bar{1}$ occur but no $31\bar{1}$; $50\bar{1}$ and $30\bar{1}$ but no $40\bar{1}$; $33\bar{2}$ and $31\bar{2}$ but no $32\bar{2}$. In fact, there is a tendency for the sum of the indices to be even, and such a selection of the simple planes as this always implies that the wrong axes have been taken.

In the B list for ZnS, indices such as $(52\bar{2})$ are intermediate between $31\bar{1}$ and $21\bar{1}$.

In the case of rock-salt, it is not possible to regard the pattern as completely characteristic of the one point system or the other. Photographs obtained using a thin section of crystal, about 1 mm. thick, cut parallel to a cube face, show a pattern very similar to that given by potassium chloride, though in no case are they so simple as the pattern given by the latter crystal; for a considerable amount of difference between the "odd" and "even" planes is also evident. A photograph taken with a section 6 mm. in thickness is more like one taken with potassium bromide or iodide, the difference between odd and even planes being more marked. In fig. 8, Plate 10, is reproduced a photograph taken with a section of rock-salt, 2·5 mm. thick, cut parallel to a face (100), and in fig. 9 its stereographic diagram. In the tables on the next page are set down the intensities of the spots when different thicknesses of crystal are used.

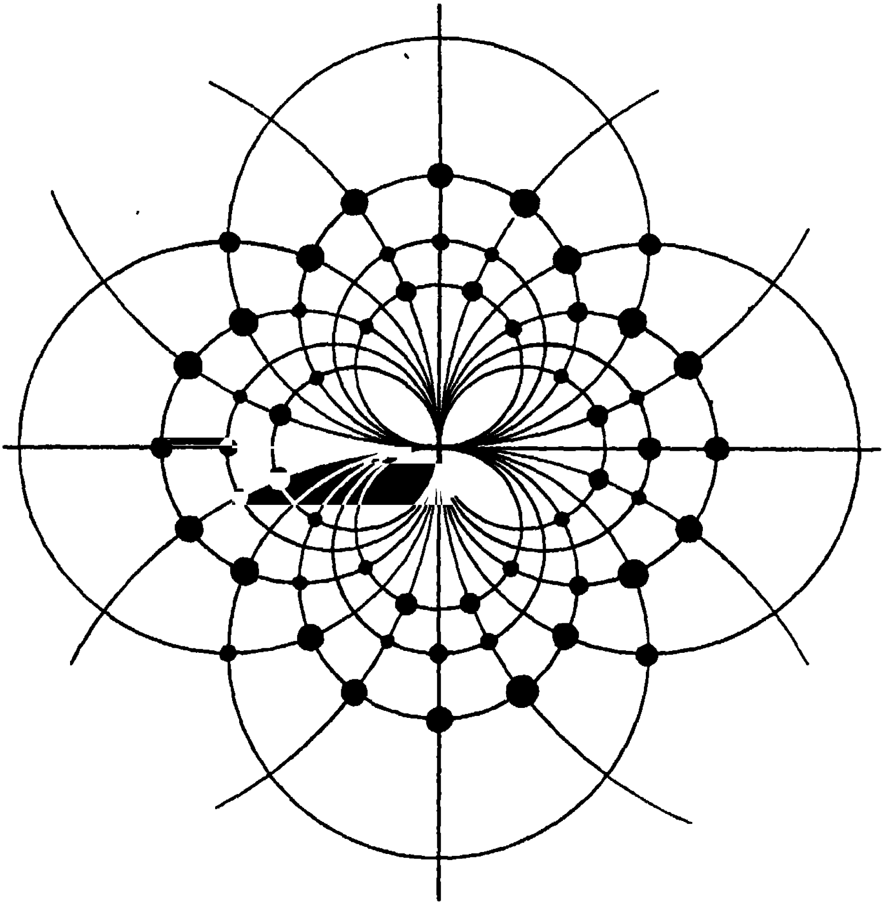

Fig. 9.—Rock-salt, 2·5 mm. thick.

Table VII.

h → 1 mm.

k ↓	0	1	2	3	4	5
0				✳	+	
1			•	✳	﹢	+
2		•	✳	✱		
3	✳	✳	✱	✱		+
4	+	﹢				
5		+		+		

NaCl, 1 mm.

Table VIII.

h → 2·5 mm.

k ↓	0	1	2	3	4	5
0				+	+	
1				✳	﹢	✱
2			•	✳		
3	+	✳	✳	﹢		﹢
4	+	﹢				
5		✱		﹢		

NaCl, 2·5 mm.

Table IX.

h → 6 mm.

k ↓	0	1	2	3	4	5
0					+	
1				+	﹢	✱
2				✳		
3		+	✳	﹢		+
4	+	﹢				
5		✱		+		

NaCl, 6 mm.

I think these tables, especially the first one, suggest that the rock-salt diffracting system is in some way intermediate between those of potassium chloride and potassium bromide. The change of intensity of the spots with the thickness of the crystal is interesting. It may be laid down as a general rule that increasing the crystal thickness increases the intensity of the inner spots as compared with that of the other. This is to be expected, for the inner spots represent the shorter and more penetrating radiations.

If in passing through a thickness dx of the crystal a proportion αdx of the radiation of a certain wave-length is reflected, and if the absorption coefficient of the radiation in the crystal is k, then the radiation reflected in a slip of crystal of thickness t will be proportional to αte^{-kt} to a rough approximation. This is a maximum when $t = 1/k$, and since α is very small, this means that to get a spot strongly marked a section of crystal should be used of such thickness that it absorbs a fraction $1/e$ of the incident radiation of that wave-length. This would explain qualitatively the variation with thickness of crystal of the intensity distribution over the spots which is actually observed.

On comparing the evidence as to the nature of the diffracting systems in these crystals of sodium chloride, and of potassium chloride, bromide, and iodide, it would seem that a very simple explanation of their curious difference may be arrived at when it is considered that in each case diffraction is caused by two different atoms, and that the relative efficiencies of the two vary from crystal to crystal. Any explanation of these differences would be an extremely improbable one which did not assume a similar structure for the whole group of alkaline halides, for these crystals resemble each other very closely in their properties. Yet it has been seen that the space lattice of diffracting points is the simple cubic one in KCl; it is the face-centred cubic lattice in KBr and KI, and that in the case of NaCl the diffracting point system is in some way intermediate between the two space lattices.

Let us consider on what atomic properties the relative efficiencies might depend. It has been firmly established that the absorption of X-rays depends on the relative proportions of the various elements contained in the absorber. It is a purely additive property of the weight of each element per cubic centimetre of the absorber, and does not depend on the manner in which the elements are combined. Also the absorption of homogeneous X-rays increases steadily with the atomic weight of the absorber, except for a sudden discontinuity consisting of a large drop in the absorption coefficient when the atomic weight of the absorber passes through that of the element of which the homogeneous X-rays are the characteristic radiation. There are, however, no discontinuities in the absorption coefficient corresponding to the changes in chemical properties of the elements in the periodic table as one passes to higher atomic weights. It is reasonable, therefore, to assume provisionally that the weight of the atom in the main defines its effectiveness as a diffracting centre, and that two atoms of equal weight are equally effective. In the case of potassium chloride the atoms of potassium and chlorine, of atomic weight 39 and 35·5 respectively, are sufficiently close in atomic weight to act as identical diffracting centres. For rock salt this is no longer true; the atomic weight of sodium and chlorine differ considerably (35·5 to 23), and complications are introduced into the simple pattern characteristic of potassium chloride. In potassium bromide and iodide one atom preponderates so greatly over the other in atomic weight that the diffracting system consists practically of atoms of one kind only, and the pattern can again be assigned to a simple space lattice, but one which is of a different nature to that of potassium chloride. Yet the atoms of alkaline metal and halogen have precisely the same arrangement in all these cases.

Let us distinguish between two kinds of diffracting points by calling them black and white. Then the points must be arranged in such a way that—

1. There are equal numbers of black and white.

2. The arrangement of points black and white taken all together is that of the first cubic space lattice.

3. The arrangement of blacks alone or of whites alone is that of the third cubic space lattice.

An arrangement which gives this result is shown in fig. 10.

In this diagram we may associate black centres with the alkaline metal, and white with the halogen, or *vice versâ*. The space lattice formed by the whites is the same as that formed by the blacks, being in each case the face-centred cube. If black and white centres become identical, as in potassium chloride, the diffracting lattice becomes the simple cubic one.

The evidence for this arrangement in the alkaline halides seems very strong, but this does not by any means complete the solution of their structure. It yet remains an open question whether one atom alone is to be associated with each point of the system, so that, for example, the black and white centres actually represent sodium and chlorine atoms in rock salt, or whether the crystal structure is of a more complex nature. It was with the object of discovering the complexity of the diffracting unit of these and other crystals that the series of crystal pattern analyses, which will now be described, were made; their results would seem to indicate clearly the association with each diffracting centre of a single atom.

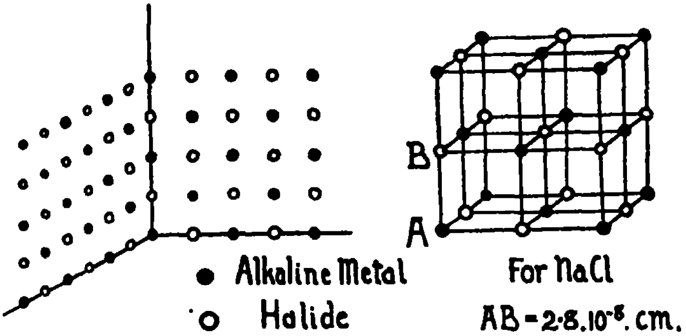

FIG. 10.

It was shown above that the stereographic diagram, giving the position of spots reflected in the planes of a trigonal rhombohedral lattice, is the same except for scale for lattices of any rhombohedral angle. The completeness with which the spots of the zincblende pattern whose projection is given in fig. 6 represent the intersections of the circles of the diagram for the trigonal lattice would suggest that in all cases in which diffracting centres were arranged on a trigonal lattice, the pattern obtained would be very much the same. At all events, this would be so when the rhombohedral angle is not very different from 60°. That this is actually the case is well shown by the stereographic projections in figs. 12 and 13. They are the projections of photographs taken with sections of fluorspar and calcite, cut perpendicular to a trigonal axis, the fluorspar photograph being given in fig. 11, Plate 10. It is clear that in this case also, as in that of zincblende, every simple plane of the lattice reflects a spot when the angle of incidence lies within a certain range. Corresponding spots in the three diagrams vary very much in intensity, but this is to be expected. The point which it is desired to make clear is the certainty with which the correct axes of the lattice may be found from a study of the pattern. In the case of fluorspar, as in that of zincblende, the rhombohedral angle of these axes is 60°. In the case of calcite it is slightly greater, a calculation of this angle and a comparison of the orientations of crystal and pattern making it clear that the axes of the lattice are three diagonals of rhombohedron faces meeting in an obtuse corner of the calcite rhombohedron, not the edges of the rhombohedron, which are generally taken as the axes to which the faces of a calcite crystal are referred.

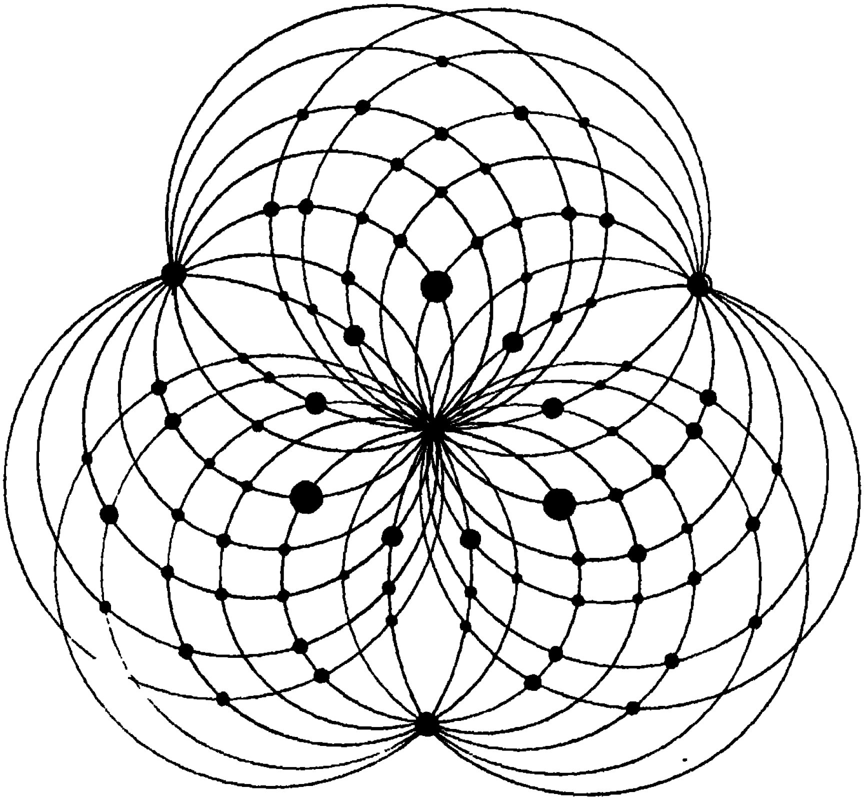

Fig. 12.—Fluorspar.

In these three cases, zincblende (ZnS), fluorspar (CaF_2) and calcite ($CaCO_3$), the diffracting centres are thus arranged on one space lattice. But, since a space lattice is an arrangement in which each point is related to its neighbours in exactly the same way as every other point, it would be impossible to arrange complex molecules in a space lattice unless only one point in each molecule is effective. It is difficult to avoid the conclusion that the molecule acts as a single point because it contains in each case one atom of much greater atomic weight than the others. A comparison with a case in which this is not so is afforded by the rock-salt pattern of threefold symmetry given in fig. 14 and Plate 10, fig. 15; it will be seen how awkwardly it fits the diagram. There is a certain want of symmetry in the figures, which must not be confused with the want of fit. Its pattern is, in fact, intermediate between that characteristic of axes of rhombohedral angle at 60° and that of axes at 90°, just as was the case with its pattern of fourfold symmetry.

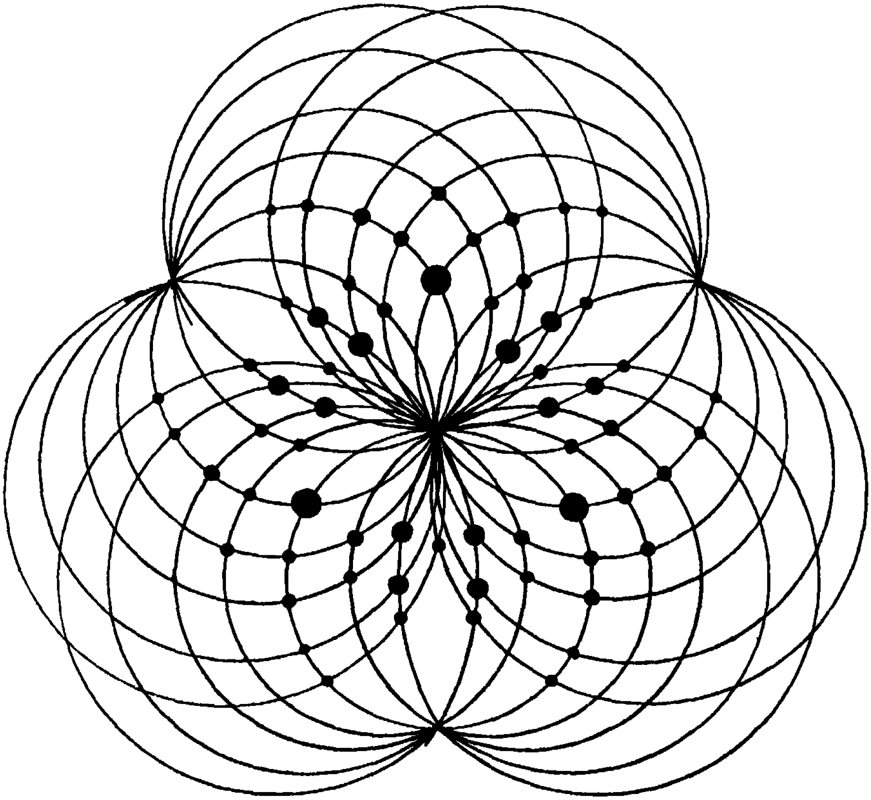

Fig. 13.—Calcite.

Having found the nature of the simple diffracting lattice in these three cases and that of the alkaline halides, the final step in the argument which would assign a single heavy atom to each diffracting centre is made below by a comparison of the scale of their lattices, that is, a comparison of the length of the sides of the elementary parallelepiped for different crystals. Since the diffraction is caused by the heavy atoms, and there is only one in each molecule, this conclusion, if correct, will mean an association of one molecule with each parallelepiped of the lattice.

In a paper to the Royal Society, read in April, 1913,* a method was described of analysing the radiations from an X-ray bulb by reflecting them from the face of a crystal, and measuring the ionisation produced by the reflected beam.

The apparatus devised for this purpose resembled a spectrometer; the crystal was set on a revolving table at the centre of the instrument, and irradiated by a narrow beam of X-rays passing through a collimator slit. The reflected beam was received, and its ionisation measured, in a chamber mounted like the spectrometer telescope. By means of this instrument it was possible to measure the strength of the reflected beam when an approximately constant beam of rays fell on the face of the crystal at varying angles of incidence. The results of the measurement made with a crystal face may be summed up in a curve, in which the strength of the

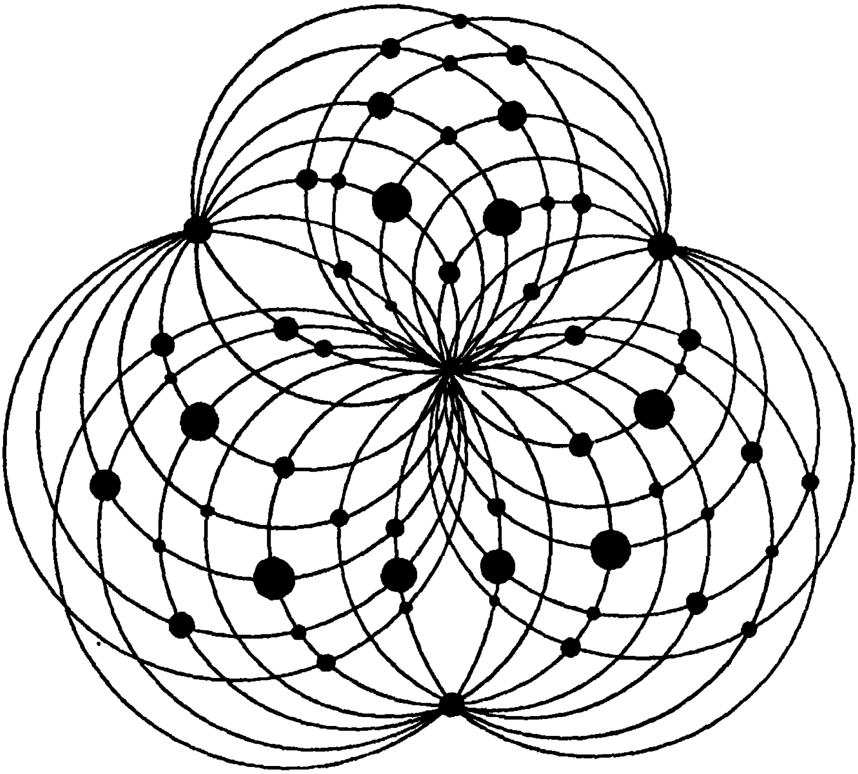

FIG. 14.—Rock-salt.

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* W. H. Bragg and W. L. Bragg, 'Roy. Soc. Proc.,' July 1, 1913.

reflected beam is plotted against the glancing angle at which the rays fell on the crystal. With most crystals, such a curve shows that at all angles there is a general reflection of the rays, the reflection being much stronger at the more glancing angles. Superimposed on this, as it were, there is at certain very sharply defined angles a special reflection of very great intensity as compared with the general reflection. This special reflection shows itself as very marked peaks on the curve, the amount of ionisation in the chamber becoming perhaps 20 times as great as the chamber is swept through the region of a peak, and then falling away to its normal value again, the whole taking place within settings a degree apart.

The results which we obtained with various crystals pointed to the existence of at least three components of the X-ray beam of definite wave-length, reflected from a crystal face when the condition

$$n\lambda = 2d\sin\theta$$

is satisfied for the component and crystal in question. Here λ is the wave-length, θ the glancing angle, and d the distance between successive planes of the crystal structure parallel to the reflecting face. The number n represents the "order" of the reflection, for several peaks, which can be recognised as belonging to the same homogeneous radiation by the identity of their absorption coefficients, appear at a series of angles whose sines are in the ratio 1 : 2 : 3.

It will possibly be objected here, that in the previous discussion of the interference patterns, the spectrum of the incident radiation has been taken to be continuous, the simplicity of the potassium chloride photograph supporting the view; while here direct evidence of the existence of homogeneous components of the radiation has been obtained. This difficulty disappears when the wave-lengths to be assigned to the spots of the interference pattern, and to the peaks of the curve, are compared. For instance, in the potassium chloride pattern of fourfold symmetry (fig. 2) the spot formed by the longest waves is reflected in the planes (221), and if a is the side of the elementary cube of the lattice of this crystal, the wave-length to be associated with the spot, from the formula

$$\lambda = 2d\sin\theta = 2a\sin^2\theta$$

is equal to $a \times 0{\cdot}22$. On the other hand, the peak corresponding to the homogeneous radiation of shortest wave-length is reflected from the face (100) of the same crystal at an angle of about 8·4°, and corresponds to a wave-length $a \times 0{\cdot}29$ nearly. The spots of the pattern thus correspond to a region of the spectrum well inside the peaks on the reflection curve, and, in general, this is true for all the patterns. The reflection curve, indeed, bears out well the assumptions as to the continuous nature of the spectrum of the radiation giving the spots, for at all angles less than 10° a strong reflection takes place which only falls away slowly as the glancing angle is increased. The very fact that in most photographs the incident rays are parallel to an axis of symmetry ensures that no important planes occur making such an angle with the primary rays as to reflect the homogeneous components.

It is possible to recognise the same three peaks, which will be referred to as A, B, C, in the curves drawn for reflection in the faces of almost all crystals which have been tried. They are always of approximately the same relative height, they have each a characteristic absorption coefficient, and they are spaced in the same way on the curves. There appears to be no doubt that three lines* exist in the spectrum of the incident radiation, which give rise to the peaks. This being so, one has a means of finding with some accuracy the ratio of the values of *d*, the distance between successive planes of the structure, for different crystals and different faces of the same crystal.

The angles at which these peaks are reflected from the various faces of a crystal, and from faces of different crystals, thus afford a great insight into the crystal structure; and, in fact, they supply just that information concerning the structure which the interference patterns do not, for by their means the dimensions of the lattices of different crystals can be accurately compared. The interference patterns only supply information concerning the nature of the lattices.

An analysis of the results obtained when different faces of the same crystal are used to reflect the X-rays in the spectrometer will show how this comparison is carried out.

In the curves for reflection from the three primary planes of the rock-salt crystal (100), (110), (111), (two of which are shown in fig. 16), the peaks occur for each face, but at different angles. From the equation

$$\lambda = 2d \sin\theta,$$

θ being the angle for the peak of the first order in each case, we have, for these three faces

$$d_{(100)} : d_{(110)} : d_{(111)} :: \frac{1}{\sin\theta_{(100)}} : \frac{1}{\sin\theta_{(110)}} : \frac{1}{\sin\theta_{(111)}},$$

where $d_{(100)}$ is the distance between planes parallel to the face (100), $\theta_{(100)}$ the angle at which the most prominent peak is reflected from the same face.

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* By using narrow slits in the reflection apparatus, evidence of the existence of more than three lines has been obtained, the B and C peaks being really double. See fig. 16.

The angles for these three faces are 11·4°, 16·0°, 9·8°, respectively. This gives the result

$$d_{(100)} : d_{(110)} : d_{(111)} :: 1 : 0·718 : 1·16,$$

whereas

$$1 : \frac{1}{\sqrt{2}} : \frac{2}{\sqrt{3}} :: 1 : 0·707 : 1·15,$$

these being the theoretical relations for the face-centred cubic space lattice. This does not comprise all the information which a study of these three curves yields, they will be analysed more carefully below. For the present, it is sufficient to indicate what strong reasons there are for assuming that the distances *d* for the various faces can be accurately compared, by finding the angles at which these peaks occur.

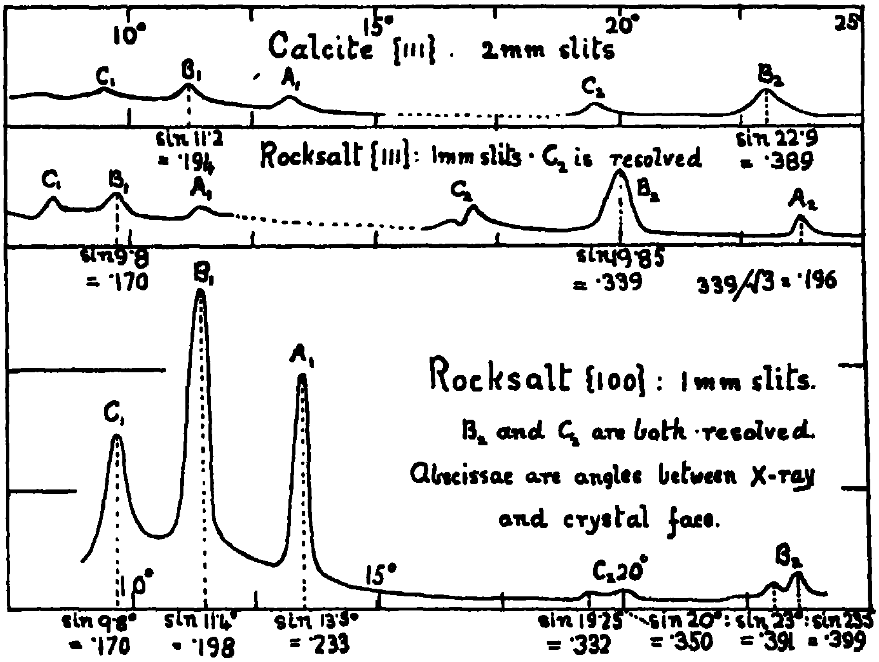

FIG. 16.

It has been seen that the patterns given by potassium chloride, zincblende, fluorspar, and calcite can be ascribed to diffraction by points of a space lattice. It is now desired to compare the dimensions of the lattices of these crystals; since the absolute value of the wave-length λ of the radiation which forms the peaks is as yet unknown, the dimensions of each lattice will be expressed in terms of λ as unit.

Since now both the form and the dimensions (in terms of λ) of the elementary parallelepiped are known, for the space lattice arrangement of diffracting centres of these crystals, it is possible to calculate the volume of this parallelepiped; the volume is that associated with each point of the lattice, it is the inverse of the number of points per unit volume. A multiplication of this volume by the density of the crystal gives the mass associated with each diffracting centre, and it is to be expected that the comparison of these masses (for different crystals) will give some idea as to whether the centre consists of atoms, molecules, or groups of molecules. The results of these calculations for the various crystals are set forth in the table below:—

In this table—

θ = glancing angle of B peak, 1st order.
d = distance between planes parallel to the face investigated.
V = volume of elementary parallelepiped, calculated from this value of d and a knowledge of the nature of the lattice.
ρ = density of crystal.
M = molecular weight of substance.

Table X.

Crystal.	Lattice.	Face.	θ.	$\frac{d}{\lambda}$.	$\frac{V}{\lambda^3}$.	ρ.	M.	$\frac{V\rho}{\lambda^3 M}$.
Sylvine, KCl	Simple cubic............	(100) (111)	10·2° 18·0	2·86 1·62	23·4 22·2	1·97	74·5	0·605
Rock-salt, NaCl...	Face-centred cubic ...	(100) (110) (111)	11·4 16·0 9·8	2·53 1·82 2·95	32·5 33·9 33·5	2·15	58·5	1·22
Zincblende, ZnS...	" " ...	(110)	16·5	1·76	30·8	4·06	97·0	1·28
Fluorspar, CaF_2 ..	" " . .	(100) (111)	11·7 10·3	2·46 2·79	29·8 28·3	3·18	78·0	1·18
Calcite, $CaCO_3$ ...	Rhombohedral	(100) (111)	10·5 11·2	2·74 2·60	44·8	2·71	100·0	1·22
Iron pyrites, FeS_2	Face-centred cubic ?*	(100)	12·1	2·39	27·3	5·03	120·0	1·15

* The interference pattern of this crystal has not yet been obtained.

The last column gives the value of $V\rho/\lambda^3 M$, the mass associated with each diffracting centre divided by the molecular weight of the substance. This quantity is, therefore, proportional to the number of molecules associated with each centre. For each of these crystals, with the exception of potassium chloride, this quantity is the same within the errors* of experiment, showing that in all these crystals the number of molecules associated with each diffracting centre is the same. Taking into consideration the very different constitution of these crystals, this fact seems to point to the association of one molecule, and one alone, with each diffracting centre; and since in zincblende, fluorspar, and calcite the molecule contains only one heavy atom, the conclusion is arrived at that the space lattice which the diffracting pattern indicates is that formed by the individual zinc or calcium atoms of these crystals.

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* It must be remembered that in calculating this quantity, any percentage error in the value for sin θ is trebled, since sin θ is raised to the third power.

Potassium chloride forms an apparent exception to this rule, for it has a value for $V\rho/\lambda^3M$ half that given by the other crystals. The reason for this is clear when it is remembered that in potassium chloride there are two atoms of very nearly equal atomic weights. Each molecule provides two diffracting centres, these being arranged on the simple cubic space lattice. The mass associated with each centre is not that of a molecule, but half of this quantity, and again it is single atoms, but now of two kinds, which form the points of the diffracting space lattice.

It is clear that the argument given here cannot pretend to be a complete proof of this important point. It is conceivable, for example, that in all these crystals it just happens that the molecules are grouped together in fours, and that these groups form the diffracting centres. It is easy to picture such an arrangement for the alkaline halides, in fact this is the arrangement given to all such binary compounds by the theory of closest packing by Pope and Barlow. Their arrangement would explain satisfactorily the patterns and peak relations of rock-salt, zincblende, and potassium bromide and iodide, for the black and white centres of the diagram given in fig. 8 are represented by tetrahedra composed of four spheres corresponding to atoms of either nature. This would also involve, however, the grouping in fours of the calcium atoms in calcite, and considerable difficulty is experienced in picturing an arrangement which does this. A similar difficulty arises in the case of fluorspar. Potassium chloride is also hard to account for on this arrangement, if it is granted that in this substance potassium and chlorine act almost identically on the X-rays, for the atoms are in the closest packed arrangement of the face-centred cube, while the diffraction pattern is characteristic of the simple cubic lattice. Many more comparisons of crystals are necessary to confirm this point, in the meantime it will be assumed that the simple structure correctly represents the truth, and that the diffracting centres are single atoms.

It has been seen how the comparison of the angles of reflection of a peak from various faces of the same crystal gives information concerning the space lattice structure of the crystal. Further information can be got by studying the dimensions of these peaks. For instance, the curves for two of the three primary planes (100), (110), (111) of rock-salt are given in fig. 16* and a reference to these curves will show the very marked difference which there is between the curves for the face (100) and that for the face (111). The (100) curve shows very marked first-order peaks, much smaller second-order peaks, and the merest indication of the peaks of the third order. The (111) curve on the other hand shows the second-order peaks very much stronger than those of the first order.

This difference of the curves corresponds to a difference in the nature of the planes parallel to these faces of the crystal. In the arrangement of black and white points given in fig. 8, it will be seen that the successive planes parallel to (100) contain equal numbers of black and white points; the same is true for the planes (110), which also give a strong first-order reflection. The planes parallel to (111), on the other hand, contain alternately all blacks and all whites. The black points alone form a face-centred lattice, for which the (111) planes are further apart than the (100) planes in the ratio $2/\sqrt{3}$. Thus the small first-order peaks reflected from the (111) face of rock-salt correspond to a periodicity of black planes alone, parallel to (111), the planes containing the heavy chlorine atoms. The presence midway between these planes of the planes containing sodium atoms does not completely destroy this reflection of the first order, but it goes a long way towards doing so, while of course the reflection of the second order is reinforced and gives a large second-order peak. This explains the abnormal relative magnitudes of the (111) peaks of different orders as compared with those reflected from the faces (100) and (110).

In accordance with this, it is found that if the sodium is replaced by potassium, the first-order peak reflected from the (111) face becomes too small to be detected, the (111) curve for sylvine appears to have a peak of the first order, at an angle corresponding to planes $1/\sqrt{3}$ as far apart as the planes parallel to (100). In fact, the peaks are where they should be for the simple cubic space lattice.

This argument may be summed up as follows: The arrangement of the heavy atoms of these crystals (potassium chloride with its two equal atoms being an exceptional case) is that of the space lattice which is the skeleton of the crystal, one molecule containing one heavy atom being associated with each point of the lattice. The first order peaks of the reflection curves are in the positions which theory would give for this space lattice, but the relative magnitudes of the peaks of the first and second orders on any curve are influenced by the positions of the lighter atoms in the crystal structure. If these lighter atoms are so disposed as to lie on the planes of the heavy atom space lattice parallel to the face investigated, then the reflection curve may be said to be of the normal type, it will have large peaks of the first order and small ones of the second. If the lighter atoms are arranged on planes situated halfway between the planes of the lattice, the first-order peaks will be diminished and those of the second order reinforced.

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* For the experimental evidence in support of this part of my argument I am indebted to my father.

The curves for the faces (100) and (111) of fluorspar show this effect in a very marked manner (fig. 17). This crystal has as its skeleton the face-centred cubic lattice, the points of the lattice being represented by the calcium atoms. The fluorine atoms are so disposed that the reflection from the (111) planes is now of the normal type, in strong contrast to the curves for rock-salt. On the other hand, the first-order reflection from the face (100) has almost disappeared. The fluorine atoms must be arranged so as to lie on or near the (111) planes of the fundamental lattice, not on the planes (100) as are the sodium atoms of rock-salt. The calcite curves given in fig. 16 show that for this crystal it is the (100) planes which give normal reflection, the curve for the face (111) being very like that for the face (111) of rock-salt.

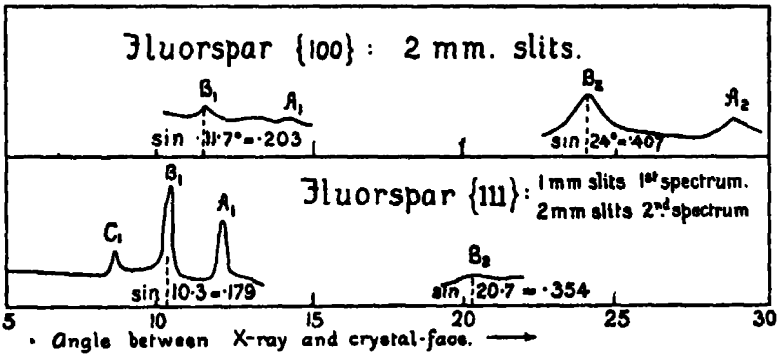

FIG. 17.

It is hoped that an examination of the reflection from various faces of all these crystals may lead to the discovery of the exact positions of the lighter atoms in the crystal structure; as yet the experimental results are very incomplete. The results obtained so far seem to fix with some certainty the arrangement of the heavy atoms of these simple crystals, and in the case of the alkaline halides it is hoped that the positions assigned to atoms of both kinds are at any rate close approximations to the truth. A slight symmetrical distortion of the arrangement, which would reduce the crystal symmetry, would not affect any of the results which have been obtained here.

The analysis of crystal structures given here was initially undertaken with the object of discovering the absolute wave-length in centimetres of the homogeneous radiations issuing from the X-ray bulb. The positions of the peaks on the curves gave the wave-length of the corresponding radiations in terms of the dimensions of the crystal space lattice. As long as the complexity of the unit associated with each point of the lattice is unknown, the absolute wave-length cannot be calculated. If the arrangement here assigned to the alkaline halides is right, the dimensions of the lattice can be given in centimetres, for the mass associated with each centre of the lattice can be calculated from the known mass in grammes of the hydrogen atom.

For rock-salt, mass of 1 molecule of NaCl $= 58{\cdot}5 \times 1{\cdot}64 \times 10^{-24}$; therefore

$$58{\cdot}5 \times 1{\cdot}64 \times 10^{-24} = V\rho = 33{\cdot}3 \times 2{\cdot}15 \times \lambda^3,$$

$$\lambda^3 = 1{\cdot}34 \times 10^{-24}, \qquad \lambda = 1{\cdot}10 \times 10^{-8} \text{ cm.}$$

From the value for λ, and that for d/λ given in Table X, the dimensions of the lattice for any crystal in this table can be calculated.

Summary.

For a number of simple crystals the interference patterns can be ascribed to diffraction of a "white" radiation by a set of points on a space lattice. Each of these points is a single atom; if one atom in the molecule is at least twice as heavy as any of the others, it is the lattice formed by these atoms alone which the diffraction pattern reveals. Two atoms of nearly the same atomic weight are nearly equivalent as diffracting centres. The lighter atoms of the molecule are not grouped closely round the heavy atom forming the diffracting space lattice, but occupy intermediate positions. For instance, in sodium chloride the sodium atom has six neighbouring chlorine atoms equally close with which it might pair off to form a molecule of NaCl. The reflection curves and interference patterns given by the alkaline halides agree in assigning the same structure to these salts, the atoms being arranged on a simple cubic space lattice in such a way that rows parallel to the cubic axes contain alternate atoms of either kind. The association of a single heavy atom with each point of the space lattice is indicated by the fact that the mass of each point is proportional to the molecular weight of the substance when each molecule contains one heavy atom. This relation is got from the reflection curves of different crystals. A knowledge of the mass of a hydrogen atom makes it possible to calculate the actual dimensions of a crystal lattice, and so to find the wave-length in centimetres of the homogeneous components of the X-ray beam, this being the object for which these analyses of crystal structure were undertaken.

Fig. 2.—Potassium chloride.

Fig. 8.—Rock-salt, 2·5 mm. thick.

Fig. 11.—Fluorspar.

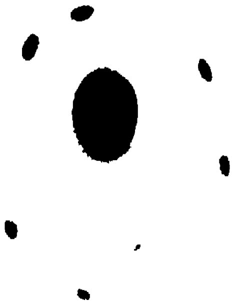

Fig. 15.—Rock-salt.

In conclusion I should like to express my indebtedness to Prof. Pope for his sympathetic interest and generous assistance. Dr. Hutchinson, with the greatest kindness, has overcome the only experimental difficulties connected with this subject by supplying the necessary crystal sections; but for his help it would have been impossible to obtain the very large number of photographs used in the investigation. These photographs were obtained at the Cavendish Laboratory, and I wish to thank Prof. Sir J. J. Thomson for his kind interest in the experiments. The measurements with the X-ray spectroscope were, as already stated, made by my father in the laboratory of the University of Leeds.

The Structure of the Diamond.

By W. H. Bragg, M.A., F.R.S., Cavendish Professor of Physics in the University of Leeds, and W. L. Bragg, B.A., Trinity College, Cambridge.

(Received July 30, 1913.)

There are two distinct methods by which the X-rays may be made to help to a determination of crystal structure. The first is based on the Laue photograph and implies the reference of each spot on the photograph to its proper reflecting plane within the crystal. It then yields information as to the positions of these planes and the relative numbers of atoms which they contain. The X-rays used are the heterogeneous rays which issue from certain bulbs, for example, from the commonly used bulb which contains a platinum anticathode.

The second method is based on the fact that homogeneous X-rays of wave-length λ are reflected from a set of parallel and similar crystal planes at an angle θ (and no other angle) when the relation $n\lambda = 2d \sin\theta$ is fulfilled. Here d is the distance between the successive planes, θ is the glancing angle which the incident and reflected rays make with the planes, and n is a whole number which in practice so far ranges from one to five. In this method the X-rays used are those homogeneous beams which issue in considerable intensity from some X-ray bulbs, and are characteristic radiations of the metal of the anticathode. Platinum, for example, emits several such beams in addition to the heterogeneous radiation already mentioned. A bulb having a rhodium anticathode, which was constructed in order to obtain a radiation having about half the wave-length of the platinum characteristic rays, has been found to give a very strong homogeneous radiation consisting of one main beam of wave-length $0{\cdot}607 \times 10^{-8}$ cm.,*, and a much less intense beam of wave-length $0{\cdot}533 \times 10^{-8}$ cm. It gives relatively little heterogeneous radiation. Its spectrum, as given by the (100) planes of rock-salt, is shown in fig. 1. It is very convenient for the application of the second method. Bulbs having nickel, tungsten, or iridium anticathodes have not so far been found convenient; the former two because their homogeneous radiations are relatively weak, the last because it is of much the same

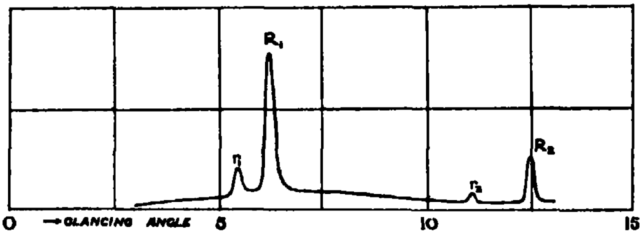

FIG. 1.—Spectra of rhodium rays : 100 planes of rock-salt.

wave-length as the heterogeneous rays which the bulb emits, while it is well to have the two sets of rays quite distinct. The platinum homogeneous rays are of lengths somewhat greater than the average wave-length of the general heterogeneous radiation; the series of homogeneous iridium rays are very like the series of platinum rays raised one octave higher. For convenience, the two methods may be called the method of the Laue photograph, or, briefly, the photographic method, and the reflection method. The former requires heterogeneous rays, the latter homogeneous. The two methods throw light upon the subject from very different points and are mutually helpful.

The present paper is confined almost entirely to an account of the application of the two methods to an analysis of the structure of the diamond.

The diamond is a crystal which attracts investigation by the two new methods, because in the first place it contains only one kind of atom, and in the second its crystallographic properties indicate a fairly simple structure. We will consider, in the first place, the evidence given by the reflection method.

The diagram of fig. 2 shows the spectrum of the rhodium rays thrown by the (111) face, the natural cleavage face of the diamond. The method of obtaining such diagrams, and their interpretation, are given in a preceding paper.* The two peaks marked R_1, r_1 constitute the first order spectrum of the rhodium rays, and the angles at which they occur are of importance in what follows. It is also a material point that there is no second order spectrum. The third is shown at R_3, r_3; the strong line of the fourth order is at R_4, and of the fifth at R_5.

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* This value is deduced from the positions of the spectra of the rhodium rays in the (100) planes of rock-salt on the assumption that the structure of rock-salt is as recently described (see preceding paper).

The first deduction to be made is to be derived from the quantitative measurements of the angle of reflection. The sines of the glancing angles for R_1, R_3, R_4, R_5 are (after very slight correction for errors of setting) 0·1456, 0·4425, 0·5941, 0·7449. Dividing these by 1, 3, 4, 5 respectively, we obtain 0·1456, 0·1475, 0·1485, 0·1490. These are not exactly equal, as they might be expected to be, but increase for the larger angles and tend to a maximum. The effect is due to reasons of geometry arising from the relatively high transparency of the diamond for X-rays, and the consequent indefiniteness of the point at which reflection takes place. The true value is the maximum to which the series tends, and may with sufficient accuracy be taken as 0·1495. In order to keep the main argument clear, the consideration of this point is omitted.

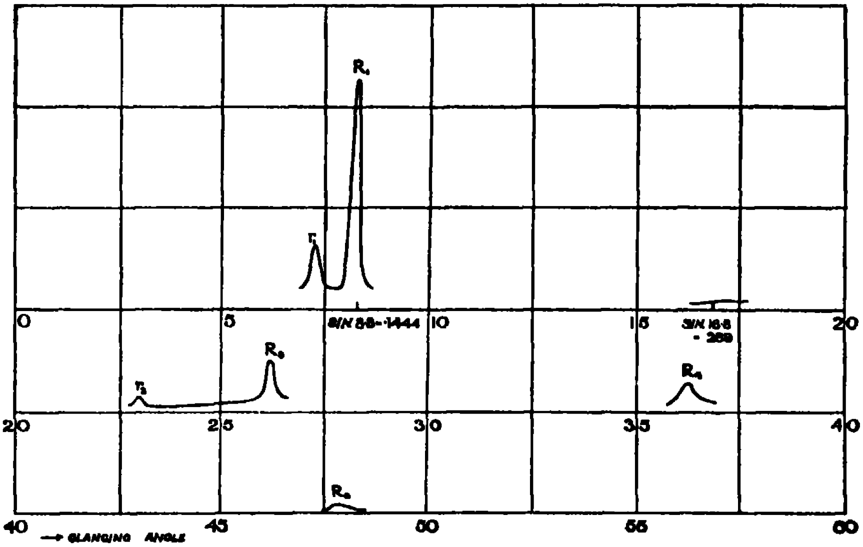

FIG. 2. Spectra of rhodium rays: 111 planes of diamond.

We can now find the distance between successive (111) planes.

We have

$$\lambda = 2d \sin\theta, \qquad 0{\cdot}607 \times 10^{-8} = 2d \times 0{\cdot}1495, \qquad d = 2{\cdot}03 \times 10^{-8}.$$

The structure of the cubic crystals which have so far been investigated by these methods may be considered as derived from the face-centred lattice (fig. 3): that is to say, the centres which are effective in causing the reflection of the X-rays are placed one at each corner and one in the middle of each face of the cubical element of volume. This amounts to assigning four molecules to each such cube, for in general one atom in each molecule is so much more effective than the rest that its placing determines the structure from our point of view. There are four, because the eight atoms at the corners of the cube only count as one, each of them belonging equally to eight cubes, and the six atoms in the centres of the faces only count as three, each of them belonging equally to two cubes. The characteristics of the reflection are then as follows:—

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* 'Roy. Soc. Proc.,' vol. 88, p. 428.

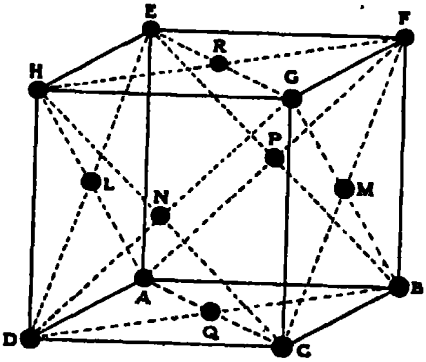

Fig. 3.

Let ABCDEFGH be the cubical element. There are effective centres at all the corners and at L, M, N, P, Q, R, the middle points of the faces. The edge of the cube being denoted by $2a$, the reflecting planes which are parallel to a cube face, called generally the (100) planes, are spaced regularly, the distance from plane to plane being a. All the planes contain equal numbers of centres.

The (110) planes, of which the plane through ACGE is a type, are regularly spaced at a distance $a/\sqrt{2}$, and also are all equally strewn with effective centres.

The (111) planes, of which the planes through EDB, HCF are types, are regularly spaced at a distance $2a/\sqrt{3}$, and again are all similar to each other.

In what may for the present be called the normal case, any one of these sets of planes gives a series of spectra which diminish rapidly in intensity as we proceed from lower to higher orders, as, for example, the spectra of the rhodium rays given by the (100) planes of rock-salt. (Fig. 1 shows the spectra of the first two orders.)

The relative spacings of the spectra given by these three sets of planes are shown in fig. 4. Spectra of the (100) planes being supposed to occur at values of sin θ proportional to 1, 2, 3, ..., it follows from the above argument that the (110) planes will give spectra at 1·414, 2·828, 4·242, ..., and the (111) planes at 0·866, 1·732, 2·598 ....

The position of the first spectrum of the (111) planes (fig. 4) is a peculiarity of the face-centred lattice. If the effective centres were at the corners only of a cube whose length of side was a, the spacings of the three sets of planes would be a, $a/\sqrt{2}$, and $a/\sqrt{3}$, and the three sets of spectra would occur at 1, 2, 3; $\sqrt{2}$, $2\sqrt{2}$, $3\sqrt{2}$; $\sqrt{3}$, $2\sqrt{3}$, $3\sqrt{3}$.

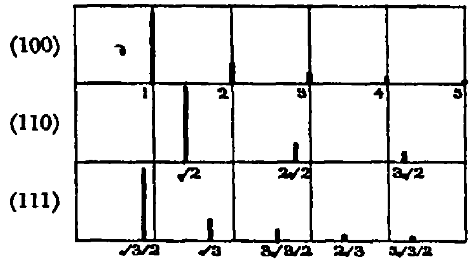

Fig. 4.—Spectra of face-centred lattice.

The cubical crystals which we have so far examined give results which resemble the diagram of fig. 4 more or less closely. Individual cases depart so little from the type of the diagram that the face-centred lattice may be taken as the basis of their structure and the departures considered to reveal their separate divergencies from the standard. For convenience of description we will speak of the first, second, third spectra of the (100) or (111) planes and so on, with reference to fig. 4. We may then, for example, describe the peculiarity of the rock-salt (111) spectrum* by saying that the first order spectrum is weak and the second strong. The interpretation (*loc. cit.*) is that the sodium atoms are to be put at the centres of the edges of the cubic element of volume, and the chlorine atoms at the corners and in the middle of each face or *vice versâ:* for then the face-centred lattice (cube edge $2a$) is brought half way to being the simple cubic lattice (edge a) having an effective centre at every corner. The first (111) spectrum tends to disappear, the second to increase in importance. In the case of potassium chloride, the atoms are all of equal weight and the change is complete: the first order spectrum of the (111) planes disappears entirely. In zincblende or iron pyrites one atom is so much more effective than the other that the diagram of spectra is much more nearly characteristic of the face-centred lattice: at least so far as regards the spectra of the lower orders. We hope to deal with these cases later.

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* See preceding paper.

Let us now consider the case of the diamond. The spectrum given by the (111) planes is shown in some detail in fig. 2. It should be stated that the ordinates represent the gross currents observed; nothing has been subtracted for natural leak, scattered radiation, and so forth.

We first use the angular measurements to enable us to determine the number of carbon atoms in the elementary cube of side $2a$. Let us assume provisionally that there are four carbon atoms to each cube, making the face-centred lattice. The density of the diamond is 3·51, and the weight of each atom is 12 times the weight of each hydrogen atom or $12 \times 1{\cdot}64 \times 10^{-24}$.

The volume of the cube is therefore

$$\frac{4 \times 12 \times 1{\cdot}64 \times 10^{-24}}{3{\cdot}51} = 22{\cdot}4 \times 10^{-24}.$$

The length of each edge (*i.e.* $2a$) will then be

$$\sqrt[3]{(22{\cdot}4 \times 10^{-24})} = 2{\cdot}82 \times 10^{-8}.$$

The distance between consecutive (111) planes

$$= 2a/\sqrt{3} = 1{\cdot}63 \times 10^{-8}.$$

Now we have found experimentally that the right value is $2{\cdot}03 \times 10^{-8}$. These two numbers are very nearly in the ratio of $1 : \sqrt[3]{2}$. It is clear that we must put eight, not four, carbon atoms in the elementary cube; we then obtain $2a/\sqrt{3} = 2{\cdot}05 \times 10^{-8}$, and this close agreement with the experimental value suggests that we are proceeding in the right way. The value of $2a$ is $3{\cdot}55 \times 10^{-8}$.

We have therefore four carbon atoms which we are to assign to the elementary cube in such a way that we do not interfere with the characteristics of the face-centred lattice.

It is here that the absence of the second order spectrum gives us help. The interpretation of this phenomenon is that in addition to the planes spaced at a distance apart $2{\cdot}03 \times 10^{-8}$ there are other like planes dividing the distances between the first set in the ratio 1 : 3. In fact there must be parallel and similar planes as in fig. 5, so spaced that $AA' = A'B/3$, and so on. For if waves fall at a glancing angle θ on the system ABC, and are reflected in a second order spectrum we have $2\lambda = 2\,AB \sin\theta$. The planes A′B′C′ reflect an exactly similar radiation which is just out of step with the first, for the difference of phase of waves reflected from A and B is 2λ, and therefore the difference of phase of waves reflected from A and A′ is $\lambda/2$. Consequently the four atoms which we have

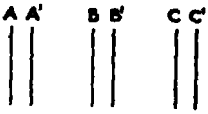

Fig. 5.

at our disposal are to make new (111) planes parallel to the old and related to them as A′B′C′ are to ABC. When we consider where they are to go we are helped by the fact that being four in number they should go to places which are to be found in the cubes in multiples of four. The simplest plan is to put them in the centres of four of the eight smaller cubes into which the main cube can be divided. We then find that this gives the right spacing because the perpendicular from each such centre on the two (111) planes which lie on either side of it are respectively $a/2\sqrt{3}$ and $\frac{1}{2}(a\sqrt{3})$, where a is the length of the side of one of the eight smaller cubes. For symmetry it is necessary to place them at four centres of smaller cubes which touch each other along edges only: *e.g.* of cubes which lie in the A, C, H and F corners of the large cube. If this is done in the same way for all cubes like the one taken as unit it may be seen on examination that we arrive at a disposition of atoms which has the following characteristics:—

(1) They are arranged similarly in parallel planes spaced alternately at distances $a/2\sqrt{3}$ and $a\sqrt{3}/2$, or in the case of the diamond $0{\cdot}508 \times 10^{-8}$ and $1{\cdot}522 \times 10^{-8}$ cm.: the sum of these being the distance $2{\cdot}03 \times 10^{-8}$ which we have already arrived at.

(2) The density has the right value.

(3) There is no second order spectrum in the reflection from (111) planes.

It is not very easy to picture these dispositions in space. But we have come to a point where we may readjust our methods of defining the positions of the atoms as we have now placed them, and arrive at a very simple result indeed. Every carbon atom, as may be seen from fig. 5, has four neighbours at distances from it equal to $a\sqrt{3}/2 = 1{\cdot}522 \times 10^{-8}$ cm., oriented with respect to it in directions which are parallel to the four diagonals of the cube. For instance, the atom at the centre of the small cube *Abcdefgh*, fig. 6, is related in this way to the four atoms which lie at corners of that cube (A, *c*, *f*, *h*), the atom at the centre of the face ABFE is related in the same way to the atoms at the centres (P, Q, R, S) of four small cubes, and so on for every other atom. We may take away all the structure of cubes and rectangular axes, and leave only a design into which no elements enter but one length and four directions equally inclined to each other. The characteristics of the design may be realised from a consideration of the accompanying photographs (figs. 7 and 8) of a model, taken from different points of view. The very simplicity of the result suggests that we have come to a right conclusion.

The appearance of the model when viewed at right angles to a cube diagonal is shown in fig. 7. The (111) planes are seen on edge, and the

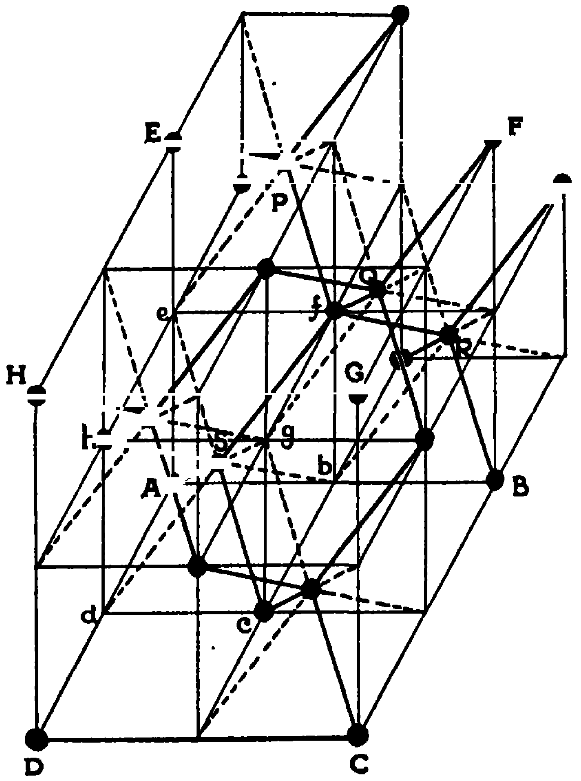

Fig. 6.

Fig. 7.—View perpendicular to a (111) axis.

Fig. 8.—The (110) planes are vertical and horizontal.

1 : 3 spacing is obvious. The union of every carbon atom to four neighbours in a perfectly symmetrical way might be expected in view of the persistent tetravalency of carbon. The linking of six carbon atoms into a ring is also an obvious feature of the structure. But it would not be right to lay much stress on these facts at present, since other crystals which do not contain carbon atoms possess, apparently, a similar structure.

We may now proceed to test the result which we have reached by examining the spectra reflected by the other sets of planes. One of the diamonds which we used consisted of a slip which had cleavage planes as surfaces; its surface was about 5 mm. each way and its thickness 0·8 mm. By means of a Laue photograph, to be described later, it was possible to determine the orientation of its axes and so to mount it in the X-ray spectrometer as to give reflection from the (110) or the (100) planes as desired.

As regards the former there should be no special features, for the four carbon atoms which we placed at the centres of four of the eight smaller cubes all now lie in (110) planes. The latter are equally spaced and all alike, the space distance being $a/\sqrt{2}$ or $1{\cdot}25 \times 10^{-8}$. The first glancing angle at which reflection occurs is, therefore, $\sin^{-1}\dfrac{0{\cdot}607 \times 10^{-8}}{2{\cdot}5 \times 10^{-8}} = 14{\cdot}15^\circ$. The experimental value was 14·35°. The spectra of higher orders occurred at 29·3° and 47·2°. The sines of these three angles are 0·2478, 0·4894, and 0·7325, or nearly as 1 : 2 : 3. Great precision was not attempted; to attain it would have been needlessly troublesome. The intensity of the different orders fell off in the usual way.

On the other hand, the (100) spectrum might be expected to show certain peculiarities. By placing four atoms at the centres of the four small cubes we have, in fact, interleaved the 100 planes, as it were: and these now consist of similar planes regularly spaced at a distance $a/2$ or $0{\cdot}885 \times 10^{-8}$. The first spectrum should therefore occur at an angle $\sin^{-1}\dfrac{0{\cdot}607 \times 10^{-8}}{1{\cdot}77 \times 10^{-8}} = \sin^{-1} 0{\cdot}343 = 20{\cdot}0$. Using the language already explained, we may say that the first (100) spectrum has disappeared, and, indeed, all the spectra of odd order. Spectra were actually found at 20·3° and 43·8°: the sines of these angles being 0·3469 and 0·6921, the latter being naturally much less intense than the former. A careful search in the neighbourhood of 10° showed that there was no reflection at all at that angle.

The results for all three spectra are shown diagrammatically in fig. 9, which should be compared with fig. 4.

It is instructive to compare the reflection effects of the diamond with those of zincblende. Our results seem to show that it is built up in exactly the same way, except that the (111) planes contain alternately zinc atoms only and sulphur atoms only. If the zinc atoms are placed at each corner of the cube and at the centre of each face, the sulphur atoms lie at four of the eight centres of the smaller cubes. The (100) planes, like the (111) planes, contain alternately zinc and sulphur atoms. These alternations of constitution modify the forms of the various spectra, so that they lie between the forms of the space-centred lattice (fig. 4) and the forms of the diamond (fig. 9). The first (100) spectrum is not entirely absent but is much smaller than the second, and in the same way the second (111) spectrum, though it is to be seen, is smaller even than the third. The scheme of the zincblende spectra is shown in fig. 10. Their actual positions agree perfectly with those which can be calculated from a knowledge of the density of the crystal, the weight of the ZnS molecule, and the wave-lengths employed. In consequence of the alternation of zinc and sulphur planes at unequal spacings along the (111) axis, the crystal ceases to be symmetrical about a plane perpendicular to that axis. It becomes hemihedral, and acquires polarity.

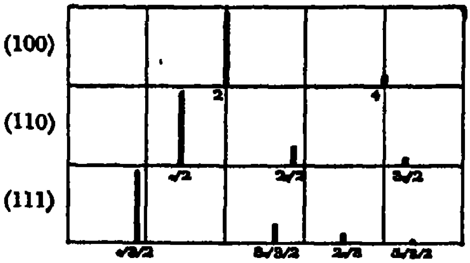

Fig. 9.—Spectra of diamond.

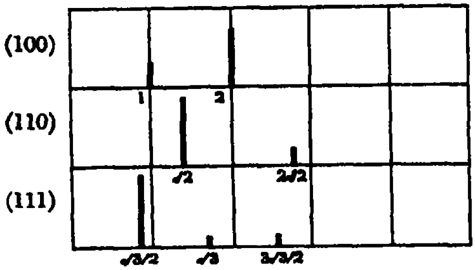

Fig. 10.—Spectra of zincblende.

We now go on to consider the Laue photograph of the diamond. A photograph taken with a section of diamond cut parallel to the cleavage plane (111) is shown in fig. 11. The experimental arrangement was similar to the original arrangement of Laue, the distance from diamond to photographic plate being 1·80 cm., and the time of exposure four hours. A test photograph was taken first, which made it possible to calculate the exact orientation to be given to the diamond in order that the incident X-rays might be truly parallel to a trigonal axis. The symmetry of fig. 11 shows that a close approximation to this orientation has been obtained. The X-ray bulb had a platinum anticathode.

Fig. 11.

In fig. 12 is given the stereographic projection of this pattern.* The spots of the photograph are represented in the diagram by dots of corresponding magnitude, and several circles, each passing through the spots reflected by the planes of one zone, are drawn. The indices placed next the spots are the Millerian indices of the planes which reflect these spots, the planes being referred to three equal axes making 60° with each other as in the case of the examples zincblende and fluorspar given in the above paper. Imagining a cube with one corner at the diamond and the long diagonal of the cube parallel to the incident X-rays, the three cube edges would meet the photographic plate at the points marked X, Y, Z. The spot (110) is thus reflected in the cube face, meeting the plate along XY, (110) being the indices of a cube face referred to the axes employed.

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* See preceding paper.

It will now be shown that on analysis the photograph appears to be in accordance with the structure which we have assigned to the diamond on the result of the reflection experiments. In the first place, of the three cubic space lattices it is evidently that which has points at cube corners and at the centres of the cube faces which is most characteristic of the diffracting system. For our purpose this space lattice is most conveniently referred to three axes which are diagonals of the cube faces meeting in a corner. The co-ordinates of any point of the system may then be written

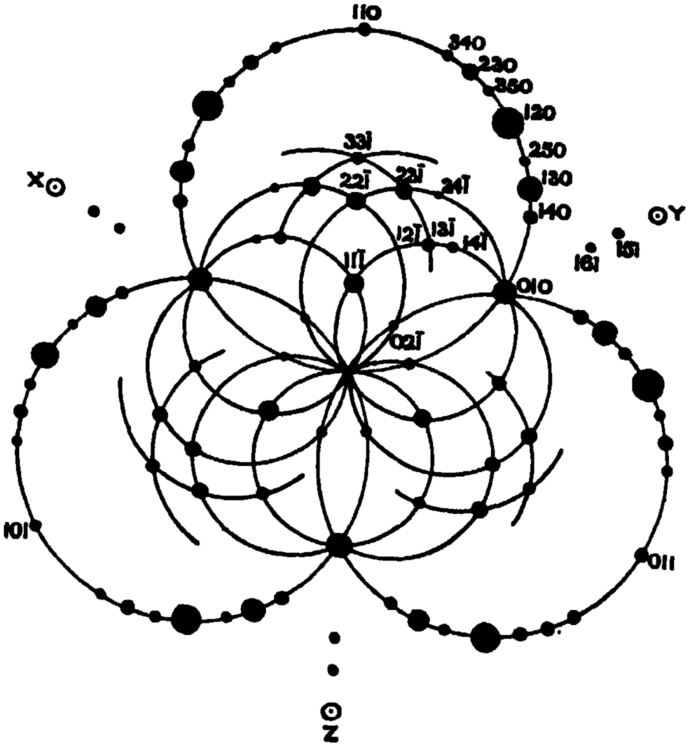

Fig. 12.

$$pc, \quad qc, \quad rc,$$

where p, q, r are any integers, positive or negative, and c is half the diagonal of the square of edge $2a$.

The indices of the reflecting plane are given for each spot of the photograph, and it will be seen that they could not possibly have a more simple form. If referred to the cubic axes they become much more complex. Along the axes chosen, the interval between successive points of the lattice is the smallest possible, and these axes are very important point-rows of the system. The remarkable series of spots lying on the three circles in the diagram which culminate at the points (110), (101), (011), are due to planes which pass through these point-rows, and this alone is good evidence of the paramount importance of the cube face diagonals as axes.

It is thus clear that a simple analysis of the pattern can be made if the planes are referred to axes of the face-centred cubic lattice. It is also evident, however, that the pattern is more complex than it should be if due to a set of identical points arranged in this lattice, of which examples have been given in a former paper. For instance, there are spots reflected by the planes $(11\bar{1})$, (131), (141), and $(22\bar{1})$, $(02\bar{1})$, and yet none by the plane $(12\bar{1})$ (see diagram, fig. 12). In the case of zincblende and fluorspar no complications of this kind occur, although in these cases the presence of the lighter atoms of sulphur and fluorine must affect somewhat the diffraction pattern given by the lattice arrangement of heavy atoms of zinc and calcium. Yet here, where carbon atoms alone are present, the pattern is not as straightforward as those given by zincblende and fluorspar. We thus come to the conclusion that the carbon atoms are not arranged on a single space lattice.

If the structure assigned to diamond in the former part of this paper is correct, a simple explanation of the diffraction pattern can be arrived at. According to this structure the carbon atoms are not arranged on a space lattice, but they may be regarded as situated at the points of two interpenetrating face-centred space lattices. These lattices are so situated in relation to each other that, calling them A and B, each point of lattice B is surrounded symmetrically by four points of lattice A, arranged tetrahedronwise and *vice versâ*. This can be seen by reference to the diagram of fig. 6.

It is now clear why the pattern must be referred to the axes of the face-centred lattice, for if the structure is to be regarded as built up of points arranged on the simple cubic lattice, with three equal axes at right angles, no fewer than eight interpenetrating lattices must be used to give all the points.

Consider lattice A referred to the cube face diagonals as axes. Then all the points of that lattice have indices

$$pc, \qquad qc, \qquad rc,$$

p, q, r being any integers. The relative position of lattice B is arrived at if we imagine lattice A to suffer a translation along the trigonal axis which is the long diagonal both of the elementary parallelepiped and of the cube, the amount of this translation being one-fourth of the long diagonal. Reference to one of the diagrams will make this more clear than any explanation which could be given here. The points of lattice B then have co-ordinates

$$(p+\tfrac{1}{4})c, \qquad (q+\tfrac{1}{4})c, \qquad (r+\tfrac{1}{4})c.$$

The planes of lattice A which have Millerian indices (*lmn*) are given by

$$lx+my+nz = \mathrm{P}c,$$

where P is any integer. The corresponding planes of lattice B are given by

$$l(x-\tfrac{1}{4}c)+m(y-\tfrac{1}{4}c)+z(n-\tfrac{1}{4}c) = \mathrm{Q}c,$$

or

$$lx+my+nz = \left(\mathrm{Q}+\frac{l+m+n}{4}\right)c.$$

When the (*lmn*) planes of both lattices are considered together, three cases present themselves :—

(1) When $l+m+n$ is a multiple of four, the planes of lattice B are coincident with those of lattice A, both being given by

$$lx+my+nz = (\text{integer} \times c).$$

An example of this is found in the plane $(1\bar{1}0)$ or (130).

(2) When $l+m+n$ is a multiple of two but not of four, the planes of lattice A are given by

$$lx+my+nz = \mathrm{P}c.$$

Those of lattice B are given by

$$lx+my+nz = (\mathrm{P}+\tfrac{1}{2})c,$$

and are thus half-way between the planes of lattice A.

Examples.—Planes such as (110) and $(12\bar{1})$.

(3) When $l+m+n$ is odd, the equations of the two sets of planes are

$$lx+my+nz = \mathrm{P}c,$$

and

$$lx+my+nz = (\mathrm{P}+\tfrac{1}{4}c),$$

or

$$lx+my+nz = (\mathrm{P}-\tfrac{1}{4})c,$$

and the planes occur in pairs, in such a way that the two planes of a pair are separated by one-fourth of the distance between the successive pairs.

Examples.—Octahedron faces (100), (010), (001), and (111).

It is now clear wherein lies the difference between planes $(11\bar{1})$ and (131), on the one hand, and $(12\bar{1})$ on the other. The $(12\bar{1})$ planes of the one lattice alone would probably give a strong reflection of a part of the X-ray spectrum in which there was a large amount of energy, but the presence half-way between them of the planes of the other lattice $(1+2-1=2)$ annuls their effect. On the other hand, though the $(13\bar{1})$ and $(11\bar{1})$ planes now occur in pairs, the wave-length reflected from them is the same as that for a single lattice. On looking over the indices of the reflecting planes, it will be seen how large a proportion of them have $l+m+n$ either odd or a multiple of four; in fact, the departure of the pattern from simplicity is just that which would be expected from the nature of the point system, which differentiates the planes into these three sets.

A more complete analysis of the pattern would be of little interest here because the positions of the reflection peaks afford a much simpler method of analysing the structure. In comparison with the examples given in the former paper, this is a case where the diffraction is caused by a point system as against a space lattice, both a translation and a rotation being necessary to bring the system into self-coincidence. This gives special interest to the photograph.

We have to thank both Prof. S. P. Thompson, F.R.S., and Dr. Hutchinson, of the Mineralogical Laboratory, Cambridge, for their kindness in lending us diamonds which were used in these experiments.

Morphological Studies in the Benzene Series. IV.—*The Crystalline Form of Sulphonates in Relation to their Molecular Structure.*

By E. H. Rodd, B.Sc., Salters' Company's Research Fellow, City and Guilds College.

(Communicated by Prof. H. E. Armstrong, F.R.S. Received July 3, 1913.)

In Part III of these studies, in which a number of isomorphous paradibromobenzenesulphonates of the rare earth metals (La, Ce, Nd, Pr, Gd, Sm) are described crystallographically,* the conclusion was arrived at that in these salts three of the benzenesulphonic groups, together with 9 or 12 molecules of water, are disposed symmetrically in a plane around a central atom of the tervalent metal. Molecular units presumably of this kind are packed together in a structure one dimension of which corresponds to the thickness of a single benzene complex observed in numerous substituted benzene derivatives, such as diiodobenzene, for example; as was pointed out, the salts under consideration may be regarded, in fact, as derived from benzene merely by the pushing apart of the zigzag columns of carbon domains, depicted by Barlow and Pope as characteristic of the hydrocarbon, in such manner as to allow of the introduction of the substituting groups present in the sulphonate in addition to benzene.

In view of this result, it was desirable to determine the crystalline structure of the acid from which the salts were derived as well as of salts containing metals of other degrees of valency. Numerous unsuccessful attempts were made to obtain measurable crystals of the paradibromo-acid; ultimately, good crystals were secured of the corresponding dichloro-acid and of its lanthanum, neodymium and praseodymium salts.

The measurements made of these salts, together with those of several related salts, are described in the following section; the issues are discussed under the headings:—

(1) The isomorphism of the dichloro- and dibromobenzenesulphonates.

(2) The morphotropic relationship of dibromobenzenesulphonates to the unsubstituted salts.

(3) The relationship of the two gadolinium *p*-dibromobenzenesulphonates

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* "Paradibromobenzenesulphonates (Isomorphous) of the 'Rare Earth' Elements—a Means of Determining the Directions of Valency in Tervalent Elements," by H. E. Armstrong and E. H. Rodd, 'Roy. Soc. Proc.,' 1912, A, vol. 87, p. 204.

($7H_2O$ and $12H_2O$) with reference to the change of structure induced by changes in the degree of hydration.

Lanthanum p-dichlorobenzenesulphonate, $La(C_6H_3Cl_2SO_3)_3.15H_2O$.—This hydrate is deposited at all temperatures between 10° and 50° C. from a solution of the salt. It consists of anorthic prisms or tables which effloresce quickly on exposure to air. The forms $a\{100\}$, $d\{101\}$ and $c\{001\}$ constitute the prism faces, the other forms developed being $e\{010\}$, $p\{01\bar{1}\}$ and occasionally $q\{\bar{1}1\bar{1}\}$. The crystal faces are never very well developed, and usually give multiple reflections. There is a distinct cleavage parallel to $a\{100\}$.

Water: Found 25·26; calculated 24·84 per cent.

System: Anorthic.

Axial ratios: $a:b:c = 1{\cdot}6193 : 1 : 1{\cdot}6028$.

$\alpha = 76° 26'$; $\beta = 113° 48'$; $\gamma = 68° 6'$.

Angle.	No. of observations.	Limits.	Mean observed.	Calculated.
100 : 101	16	53° 12′—54° 7′	53° 44′	—
101 : 001	13	56 28—57 14	56 49	56° 47′
001 : $\bar{1}$00	20	69 1—70 0	69 29	—
100 : 010	14	71 24—72 21	71 46	—
010 : $\bar{1}$10	7	37 47—38 22	38 6	—
$\bar{1}$10 : $\bar{1}$00	7	69 37—70 28	70 8	70 8
001 : 010	7	84 5—84 32	84 14	84 18
010 : 00$\bar{1}$	7	95 42—96 2	95 49	95 42
101 : 010	5	68 30—68 43	68 36	—
010 : $\bar{1}1\bar{1}$	1	——	43 5	43 3
$\bar{1}1\bar{1}$: $\bar{1}0\bar{1}$	1	——	68 19	68 21
001 : $\bar{1}$10	2	70 41—70 56	70 49	70 59
$\bar{1}$10 : $\bar{1}0\bar{1}$	2	36 20—36 48	36 34	36 39
$\bar{1}0\bar{1}$: 00$\bar{1}$	2	72 29—72 40	72 34	72 22

Neodymium p-dichlorobenzenesulphonate, $Nd(C_6H_3Cl_2SO_3)_3.12H_2O$.—This hydrate is deposited when an aqueous solution of the salt is allowed to crystallise at any temperature between the ordinary and 50° C. It forms rose-coloured, short, thick or flat prisms, the prism zone consisting of the forms $l\{010\}$, $m\{110\}$ and $n\{120\}$; the faces upon this zone are always much striated and give multiple reflections. The facets at the ends of the prism, consisting of the forms $r\{011\}$ and $o\{\bar{1}01)$, are beautifully developed and give good single images (see fig. 1).

The crystals are closely isomorphous with those of the gadolinium salt, $Gd(C_6H_3Br_2SO_3)_3.12H_2O$; but the two salts differ slightly, thus:

(1) whilst the gadolinium salt has a tabular habit, the neodymium salt is prismatic, being elongated in the direction of the c axis;

(2) the form $\{120\}$ is occasionally developed in the neodymium salt but not in the gadolinium salt, in which the form $\{130\}$ is sometimes present.

Water: Found 21·00; calculated 20·89 per cent.
System: Monosymmetric.
Axial ratios: $a:b:c = 0·5872:1:0·3810$. $\beta = 76° 34'$.

Angle.	No. of observations.	Limits.	Mean observed.	Calculated.
$010:011$	15	69° 34′—69° 45′	69° 40′	—
$011:0\bar{1}1$	7	40 37—40 47	40 41	40° 40′
$010:120$	8	40 31—42 27	41 17	41 12
$110:011$	14	68 46—68 50	68 48½	—
$011:\bar{1}01$	14	41 6—41 12	41 10½	41 10½
$\bar{1}01:\bar{1}\bar{1}0$	14	69 58—70 4	70 1	—
$010:\bar{1}01$	4	89 55—90 4	90 0	90 0

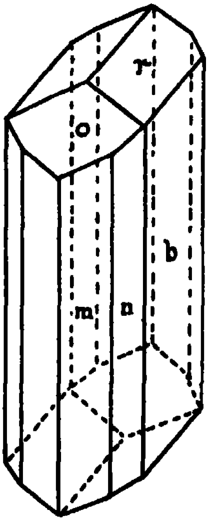

FIG. 1.—$Nd(C_6H_3Cl_2SO_3)_3.12H_2O$.

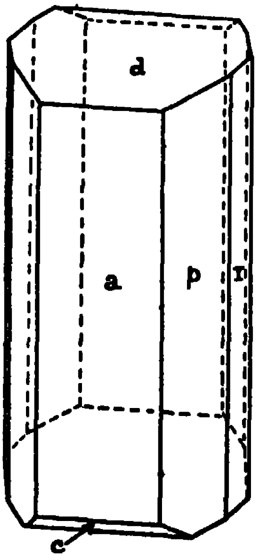

FIG. 2.—$Gd(C_6H_3Br_2SO_3)_3.7H_2O$.

Praseodymium p-dichlorobenzenesulphonate, $Pr(C_6H_3Cl_2SO_3)_3.12H_2O$.—This hydrate, like that of the corresponding neodymium salt with which it is isomorphous, is deposited at temperatures between 10° and 50° C. The crystals, which are of a pale green colour, resemble those of the neodymium salt in habit but are not so well developed. The zone [010:120:110] is invariably badly striated.

Water: Found 20·71; calculated 20·81 per cent.
System: Monosymmetric.
Axial ratios: $a:b:c = 0·5887:1:0·3819$. $\beta = 76° 26'$.

Angle.	No. of observations.	Limits.	Mean observed.	Calculated.
$010 : 011$	21	69° 24′—69° 57′	69° 38′	—
$011 : 0\bar{1}1$	9	40 27 —40 53	40 43	40° 44′
$110 : 011$	10	68 24 —68 48	68 40	—
$011 : \bar{1}01$	11	41 8 —41 32	41 18	—
$\bar{1}01 : \bar{1}\bar{1}0$	9	69 48 —70 28	70 5	70 7
$010 : 120$	3	41 1 —41 30	41 14	41 9
$120 : 110$	1	——	19 10	19 4
$110 : 1\bar{1}0$	3	59 25 —59 34	59 29	59 34

$Pr(C_6H_3Cl_2SO_3)_3.15H_2O$.—When a strong, apparently supersaturated solution of praseodymium *p*-dichlorobenzenesulphonate was allowed to crystallise spontaneously at room temperature, on two occasions, together with the massive crystals of the dodecahydrate, a few smaller crystals were obtained in the form of hexagonal plates: when examined these were found to be anorthic and closely isomorphous with the salt $La(C_6H_3Cl_2SO_3)_3.15H_2O$ they must be taken, therefore, to contain $15H_2O$, although they have not been obtained in sufficient quantity for analysis. Like the crystals of the corresponding Lanthanum salt, they gradually become opaque when kept. The crystals were so poorly developed that a complete examination could not be made. A corresponding hydrate of the neodymium salt has not been observed. When the crystals are allowed to remain in contact with the solution they are gradually converted into the dodecahydrate.

Gadolinium p-dibromobenzenesulphonate, $Gd(C_6H_3Br_2SO_3)_3.7H_2O$.—This hydrate was described in Part III of these studies but crystals have been obtained only recently on which the forms were developed that are necessary for the determination of the axial ratios. These were deposited from water at 45° C. The heptahydrate forms very massive monosymmetric prisms; the faces are always striated and seldom give good reflections. The forms generally occurring are $a\{100\}$, $p\{110\}$, $r\{120\}$ and $d\{101\}$. Another form is required for the complete determination of the crystal constants; on a few occasions $e\{\bar{1}01\}$ was observed and still more rarely $m\{122\}$ The crystals are elongated in the direction of the c axis. There is a perfect cleavage parallel to $a\{100\}$ (see fig. 2).

System: Monosymmetric.

Axial ratios: $a:b:c = 1\cdot2595:1:0\cdot6031$. $\beta = 89° 16'$.

Angle.	No. of observations.	Limits.	Mean observed.	Calculated.
100 : 110	14	51° 17′—51° 55′	51° 38′	—
110 : 120	7	16 21—17 2	16 47	16° 48′
100 : 120	8	68 12—68 41	68 20	68 21
120 : $\bar{1}$20	4	42 58—43 29	43 15	43 18
100 : 101	14	63 14—64 19	63 49	—
101 : $\bar{1}$01	5	50 28—51 35	51 11	—
$\bar{1}$01 : $\bar{1}$00	4	64 28—65 13	64 38	65 0
110 : 101	5	74 11—74 33	74 22	74 5
120 : 101	5	80 20—80 58	80 44	80 38
101 : 122	3	81 45—32 6	81 54	32 24
100 · 122	3	77 42—77 45	77 44	77 48

Didymium benzenesulphonate, $Di(C_6H_5SO_3)_3.9H_2O$.—This hydrate has been described by Holmberg but not measured.* It is very soluble in water and generally separates from the aqueous solution as a crystalline mass; a few measurable crystals were obtained from a mixture of aqueous alcohol and ethylic acetate in the form of very thin hexagonal shaped plates. Water was estimated in the salt crystallised from this solution: found 20·74 per cent.; calculated for $Di(C_6H_5SO_3)_3.9H_2O$, 20·90 per cent.

The most prominent form on the crystals is *a*{100}; other forms developed are *r*{101}, *o*{111}, and more rarely *p*{322}. Measurable crystals were difficult to obtain and were always imperfect. The cleavage is parallel to *a*{100} (see fig. 3).

System: Orthorhombic. Axial ratios: $a:b:c$ = 2·0795 : 1 : 1·9374.

Angle.	No. of observations.	Limits.	Mean observed.	Calculated.
100 : 101	11	46° 32′—47° 30′	47° 2′	—
101 : $\bar{1}$01	6	85 14—86 48	85 51	85° 56′
100 : 111	7	66 40—66 57	66 52	—
111 : $\bar{1}$11	3	46 16—46 24	46 18	46 16
100 : 322	3	57 9—57 33	57 24	57 20
101 : 111	3	54 25—54 38	54 31	54 48

The Isomorphism of Dichloro- and Dibromobenzenesulphonates.—From the measurements given above, it is obvious that praseodymium and neodymium *p*-dichlorobenzenesulphonate dodecahydrate are very closely isomorphous with gadolinium *p*-dibromobenzenesulphonate dodecahydrate. This relationship is of prime importance as proof that the three metals and the two halogens respectively are mutually displaceable in such salts. The following values speak for themselves:—

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* 'Zeit. anorg. Chem.,' vol. 53, p. 83.

Salt.	Axial ratios. $a : b : c$	β.	Equivalence parameters. $x : y : z$
$Gd(C_6H_3Br_2SO_3)_3.12H_2O$	0·5952 : 1 : 0·3817	76° 48′	6·1415 : 10·3885 : 2·6257
$Nd(C_6H_3Cl_2SO_3)_3.12H_2O$	0·5872 : 1 : 0·3810	76 34	6·0921 : 10·3750 : 2·6352
$Pr(C_6H_3Cl_2SO_3)_3.12H_2O$	0·5887 : 1 : 0·3819	76 26	6·0968 : 10·3598 : 2·6376

Attention may be specially directed to the fact that the z parameter has a value very closely approximating to the value 2·642 observed in *p*-diiodobenzene, which is characteristic, according to the Barlow-Pope hypothesis, of the rhombohedral marshalling in benzene derivatives generally.

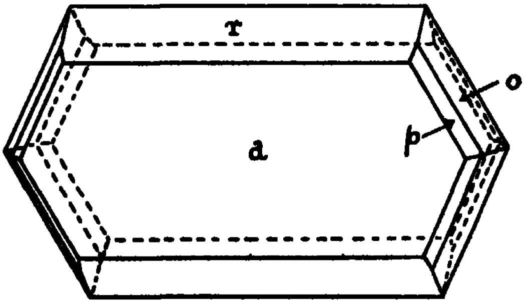

FIG. 3.—$Di(C_6H_5SO_3)_3.9H_2O$.

Morphotropic Relationship of Substituted and Unsubstituted Benzenesulphonates.—It is to be expected that didymium benzenesulphonate, which crystallises with nine molecules of water, would bear a close relationship to the corresponding neodymium salt, $Nd(C_6H_3Br_2SO_3)_3.9H_2O$. This expectation is fully realised. The benzenesulphonate is orthorhombic, the axial ratios being

$$a:b:c = 2·0801:1:1·9374,$$

whilst the neodymium *p*-dibromobenzenesulphonate is also orthorhombic

$$a':b':c' = 1·3990:1:0·8789.$$

When the crystals of the two salts are compared, two significant facts are noticeable: firstly, that the ratio $a':b'$ is almost exactly two-thirds of $a:b$; secondly, that angles on one of the corresponding zones of the two crystals are practically identical. Thus, in the case of the didymium benzenesulphonate, we have

$$\{100\}:\{101\} = 47° \ 2',$$

and in that of the dibromobenzene sulphonate

$$\{100\}:\{301\} = 46° \ 42'.$$

If in the benzenesulphonate {101} be changed to {301} and at the same time the ratio $a:b$ be multiplied by two-thirds, the axial ratios of the salt become

$$a:b:c = 1{\cdot}3868:1:0{\cdot}8611,$$

i.e. almost identical with those of the neodymium *p*-dibromobenzenesulphonate. Moreover, the pseudo-trigonal character of the salt is revealed, as the ratio $c:b$ is very nearly equal to the value 0·866 : 1, characteristic of trigonal symmetry.* The equivalence parameters of the benzenesulphonate deduced from the actual ratios thus arrived at, in comparison with those of the neodymium *p*-dibromobenzenesulphonate, are as follows :—

	x	y	z
$Nd(C_6H_3Br_2SO_3)_3.9H_2O$	2·6475 :	5·6773 :	9·9796
$Di(C_6H_5SO_3)_3.9H_2O$	2·6502 :	5·7327 :	9·8729

The close similarity between the structures of the two salts is immediately obvious from these figures.†

Relationships Consequent on Changes in the Degree of Hydration of Sulphonates.—The relationship between the dodecahydrates of gadolinium *p*-dibromobenzenesulphonate and the nonahydrate of dibromobenzenesulphonate of several other metals was discussed in the previous communication. The heptahydrate now described is apparently very different in form. It crystallises in the monosymmetric system, the axial ratios being

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* *Cf.* Part III, p. 213.

† In calculating the equivalence parameters of the acid, it is necessary first to modify the axial ratios by multiplying a by three-quarters and c by 2. As objection is sometimes made to this mode of treatment by those who do not clearly appreciate the flexible character of axial ratios, it may be as well to refute these objections here. The axial ratios of a crystal may be defined as the relative distances from the centre of the crystal at which the form which is designated (111) cuts the three axes. In all systems but the cubic, the choice of (111) is to a certain extent arbitrary : the lower the symmetry of the system, the wider is the range of choice. For instance, in the case of the monosymmetric sodium *p*-dichlorobenzenesulphonate described in this paper, there was a wide choice : a particular form was chosen as (111) and others then became (322) and (122) ; but there was no reason why either of these others should not have been made (111) ; if (322) had been called (111), the axial ratio $a:b$ would have had two-thirds its present value. Moreover, we are at present entirely ignorant of the causes determining what particular forms shall develop on the crystal and there is no *a priori* reason why these should always be the simplest possible forms. In view of these considerations it is not therefore surprising that in most cases, when dealing with orthorhombic and monosymmetric crystals, some slight modification of the interpretation originally given to the measurements is necessary, in order that morphotropic relationships between different substances may be revealed in the equivalence parameters.

Without guidance from previous knowledge and a general idea of the relationship sought, it would be impossible to discover the morphotropic relationships pointed out in this paper. Fortunately Barlow and Pope have worked out the structure of crystalline benzene on incontrovertible evidence and a relationship to benzene is first looked for. When this is found, it is generally accompanied by other significant relationships which serve to enhance the probability of the correctness of the results obtained. This was particularly well illustrated in the case of the acid and salt just discussed, as the very close structural relationship of acid to salt is apparent only when the x parameters of the two agree with the z parameter of rhombohedral benzene.

$$a:b:c = 1{\cdot}2595:1:0{\cdot}6031;\ \beta = 89^\circ\ 16'.$$

The markedly pseudo-trigonal structure, which was a feature of the nona- and dodeca-hydrates, is no longer apparent; this is to be expected, as the number 7, the number of molecules of water contained in the salt, is incompatible with three-fold symmetry. When the equivalence parameters of the salt are calculated, the axial dimension b being doubled, the following values are obtained:—

$$x:y:z = 5{\cdot}7160:9{\cdot}0768:2{\cdot}7373.$$

The z parameter approaches closely that of crystalline benzene, 2·780; it therefore appears probable that this salt may be derived from the benzene structure of hexagonal marshalling ($z = 2{\cdot}780$), and not from the alternative rhombohedral marshalling ($z = 2{\cdot}64$ about), as are the other salts. From the general similarity of the parameters of the heptahydrate to those of the other hydrates, it is to be inferred, however, that the molecules of all these salts have very similar configurations, and differ merely in being derived from the two forms of benzene, the difference being due, therefore, only to the manner in which the successive layers of molecules are superimposed one upon another.

The Relationship in Crystalline Form of p-Dichlorobenzenesulphonic Acid and the Sulphonates of Tervalent Metals.

In view of the conclusions arrived at in the previous sections and in Part III of these studies, it appears probable that the crystalline structure of the rare earth salts generally of benzenesulphonic acid and its halogen derivatives always conforms to one type, the type being one in which three sulphonic groups are symmetrically arranged around a central atom of the metal. In the case of such salts, the arrangement must be largely determined by the metal; in the case of the acid, the attractive tendencies of the constituent radicles are chiefly operative: as chemical methods throw but little light on such a problem, the study of crystalline form becomes of special importance, as a means of determining the directions in which the forces act in the formation of solids.

p-Dichlorobenzenesulphonic Acid, $C_6H_3Cl_2SO_3H.3H_2O$.—Crystals are best grown from a solution containing a little sulphuric acid, which reduces the solubility of the sulphonic acid considerably. The crystals are usually aggregates of prisms, rarely separate. The prism zone is made up of the forms *l*{010}, *r*{110} and *a*{100}, the last being sometimes undeveloped. The prism end is formed by the two faces of the form *p*{011} (see fig. 4).

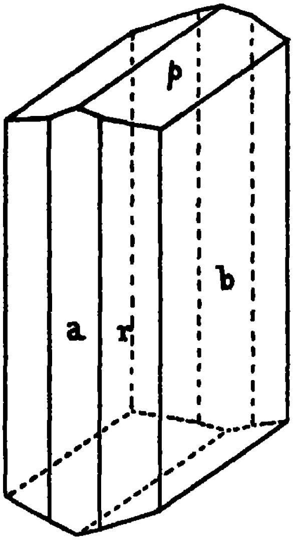

FIG. 4.—$C_6H_3Cl_2SO_3H.3H_2O$.

System: Monosymmetric.
Axial ratios: $a:b:c = 0·6255:1:0·2918$. $\beta = 79°\ 36'$.

Angle.	No. of observations.	Limits.	Mean observed.	Calculated.
$010:110$	25	58° 12′— 58° 40′	58° 24′	—
$110:1\bar{1}0$	10	62 47 — 63 25	63 18	63° 12′
$110:100$	9	31 24 — 31 50	31 36	31 36
$010:011$	13	73 48 — 74 10	73 59	—
$011:0\bar{1}1$	5	31 49 — 32 10	32 0	32 2
$110:011$	5	72 52 — 73 7	73 0	—
$011:\bar{1}10$	5	106 53 —107 14	107 2	107 0
$\bar{1}10:011$	6	90 1 — 90 30	90 17	90 11
$011:1\bar{1}0$	6	89 33 — 89 55	89 43	89 49

As the *p*-dibromobenzenesulphonates of La, Nd and Pr crystallise with nine molecules of water—three molecules per acid radicle—they are the salts with which the acid can best be compared, as no *p*-dichlorobenzenesulphonates containing this proportion of water are known.

On contrasting the axial ratios

	a	*b*	*c*
$La(C_6H_3Br_2SO_3)_3.9H_2O$ (orthorhombic)	1·3965	1	0·8753
$H(C_6H_3Cl_2SO_3).3H_2O$ (monosymmetric)	0·6255	1	0·2918

it is obvious that the ratio $c:b$ of the salt is exactly thrice that of the acid. This result is of special importance, inasmuch as each group in the molecule of the acid is repeated three times in that of the salt, the valency volume of the latter being therefore three times that of the acid. When the equivalence parameters of the acid are calculated and compared with those of the salt the following values are obtained :—

	W	x	y	z
$H(C_6H_3Cl_2SO_3).3H_2O$	50	2·6763 :	5·7050 :	3·3296
$La(C_6H_3Br_2SO_3)_3.9H_2O$	150	2·6480 :	5·6885 :	9·9582

It can be seen that the dimensions of the assemblage are practically identical in two directions and that the third dimension is exactly three times as great in the salt as in the acid. The significance of the values given under x will be obvious.

If as the crystal unit of the acid we take that of three molecules having a valency volume equal to that of the salt and calculate the equivalence parameter of the acid on this basis, values are obtained which are immediately comparable with those of the salt, viz.,

$$x:y:z = 2·6763 : 5·7013 : 9·9880.$$

In other words it appears to be legitimate to assume that the crystalline structure of the acid is pseudo-trigonal like that of the salt of a tervalent metal—that is to say, *that three molecules of acid act in conjunction.* If such be the case, the formation of the salt from the acid involves merely the displacement of three adjacent hydrogen atoms, each of unit volume, by a single atom of metal of three times the volume valency of the hydrogen atom. The fact that the symmetry is changed from monosymmetric to orthorhombic in the passage from acid to salt is proof that the equivalence though not absolute is very close; apparently the metal has the effect of rendering the arrangement slightly more symmetrical.

Assuming, in the case of the acid, that the molecules are disposed in groups of threes, the crystalline form is evidence of an attractive influence exerted at the moment of crystallisation, if not in the solution, which causes the sulphonic radicles to set radially, so that a mass of the acid (or of the salt of a rare earth metal) can be regarded as a mosaic of triangular groups each of which has its centre occupied by three sulphonic radicles.

Further justification of these conclusions is afforded by the following argument: The structure assigned by Barlow and Pope to the form of benzene in which the crystal units are packed together in rhombohedral marshalling is that given in fig. 5. Such a structure has rhombohedral symmetry, the point O, around which are grouped three small or hydrogen spheres, being an unique point of the structure from which emerges a trigonal axis perpendicular to the plane of the paper. For the present purpose it is sufficient to consider only the three benzene units outlined in the figure which are disposed symmetrically about the point O. If the three hydrogen spheres at O be removed in order to make room for three sulphonic groups, the whole structure is expanded; if the expansion take place symmetrically, so as to make room for three sulphonic groups together with nine molecules of water, the structure would assume the appearance shown diagrammatically in fig. 6. This figure is drawn strictly to scale, the shaded area representing the space which would be occupied by the acid groups and the water assuming that no expansion took place in a direction perpendicular to the plane of the paper. The heavily outlined figure therefore represents the crystal unit of the acid or of a "corresponding" salt. It is highly probable that when such units are packed together, they are more or less compressed in one direction or another according to the nature of the radicle at O and that the crystal retains trigonal symmetry more or less completely according to the influences at work at each centre. Presumably the complex would assume an approximately triangular shape through compression and its outline would be approximately such as is represented by the broken line triangle. In constructing the diagram the figure was drawn to scale, using the x and y values of benzene in deducing the hydrocarbon areas and assigning to the shaded space an area (the valency volume

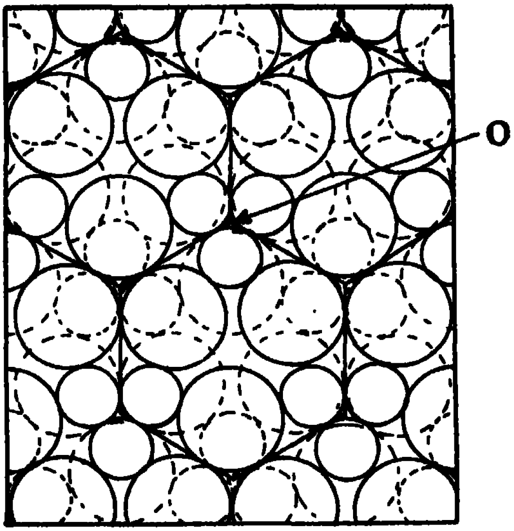

Fig. 5.

divided by the vertical dimension of rhombohedral benzene, $z = 2{\cdot}64$) corresponding to the valency volume of the sulphonic groups, the metal and the nine molecules of water. In drawing the triangle subsequently, the areas cut off were balanced against those included outside the figure. It is very noteworthy that the length AD in the figure thus constructed is practically identical with the y value of the acid referred to three molecules; also that the length AF is that of the z value.

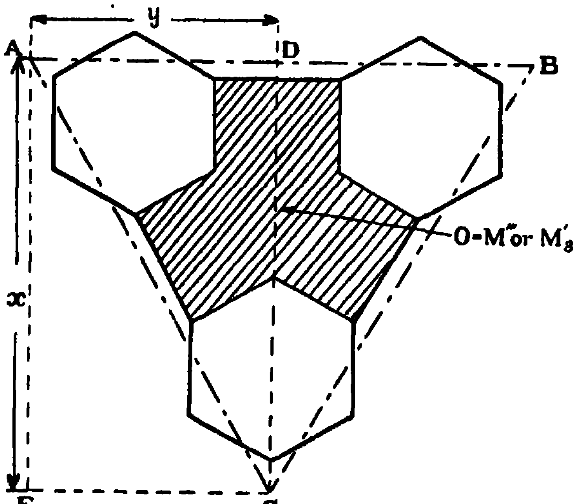

Fig. 6.

The Influence of Monad and Dyad Metals on the Crystalline Structure of Benzenesulphonates.

In this section measurements are given of the potassium, sodium and zinc salts of *p*-dichlorobenzenesulphonic acid. The results are discussed together with those obtained by Weibull,[*] who has measured a large number of benzenesulphonates and tolueneparasulphonates.

Potassium p-dichlorobenzenesulphonate, $C_6H_3Cl_2SO_3K$.—This salt was described by Lesimple[†] as crystallising with one molecular proportion of water. I find it to be anhydrous. It crystallises from water at temperatures from 20° to 37° C. in thin monosymmetric prisms; as a general rule, each prism consists of two individuals twinned on $a\{100\}$. The twin plane is a good plane of cleavage. The face $a\{100\}$ is always badly striated and useless for purposes of measurement but the a face obtained by cleavage gives good reflections. The forms *p*{110} and *r*{122} give brilliant reflections; *d*{102} is sometimes developed, but usually as a mere line (see fig. 7).

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[*] 'Zeit. Kryst. Min.,' vol. 15, p. 234.

[†] 'Zeit. Chem.,' 1868, p. 226.

Potassium: found 14·78; calculated, 14·75 per cent.

System: Monosymmetric.

Axial ratios: $a:b:c = 1·5054:1:0·7636$. $\beta = 83° 27\frac{1}{2}'$.

Angle.	No. of observations.	Limits.	Mean observed.	Calculated.
$1\bar{1}0 : 110$	19	112° 20′—112° 34′	112° 28′	—
$110 : \bar{1}10$	18	67 25 — 67 51	67 33	67° 32′
$100 : 110$	4	56 13 — 56 16	56 14	56 14
$122 : \bar{1}10$	12	70 45 — 71 9	70 54	—
$\bar{1}10 : \bar{1}22$	6	109 1 —109 13	109 8	109 6
$122 : 122$	9	71 9 — 71 20	71 13	—
$100 : 122$	12	73 15 — 73 48	73 33	73 37
$110 : 122$	6	50 5 — 50 14	50 9	50 9
$122 : \bar{1}\bar{1}0$	6	129 44 —130 0	129 49	129 51
$100 : 102$	1	——	69 53	69 42

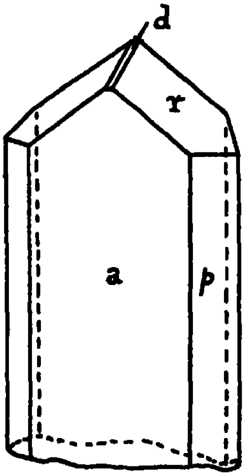

FIG. 7.—$C_6H_3Cl_2SO_3K$.

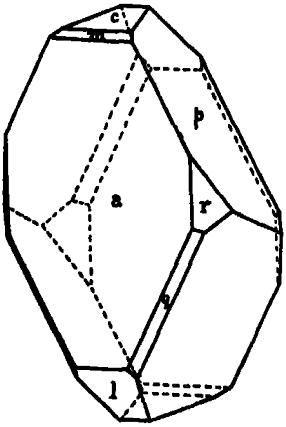

FIG. 8.—$C_6H_3Cl_2SO_3Na.H_2O$.

Sodium p-dichlorobenzenesulphonate, $C_6H_3Cl_2SO_3Na.H_2O$.—This monohydrate was described by Lesimple. I have obtained another hydrate which forms massive crystals which effloresce with great rapidity in air.

Measurable crystals of the monohydrate were obtained from aqueous solutions at 37° C. It forms massive plates or oblique six-sided tables growing upon the form *a*{100}. The other forms observed were *c*{001}, *l*{101}, *m*{$\bar{1}$02}, *r*{110}, *p*{122}, *q*{322}. There is a perfect cleavage parallel to *a*{100} from which form an optic axis emerges perpendicularly. The larger crystals appear from the analytical results to enclose water (see fig. 8).

Water: found 7·25 per cent.; $C_6H_3Cl_2SO_3Na.H_2O$ requires 6·75 per cent.

Sodium: found, in anhydrous salt 9·21 per cent.; $C_6H_3Cl_2SO_3Na$ requires 9·23 per cent.

System: Monosymmetric.

Axial ratios: $a:b:c$ = 3·0529 : 1 : 1·9583. β = 88° 46′.

Angle.	No. of observations.	Limits.	Mean observed.	Calculated.
100 : 101	15	56° 22′ — 56° 35′	56° 27′	—
101 : 001	13	32 20 — 32 32	32 26	32° 19′
100 : 001	11	88 37 — 88 55	88 50	88 46
001 : $\bar{1}00$	12	91 2 — 91 12	91 7	91 14
001 : $\bar{1}02$	4	17 49 — 18 2	17 55	17 54
$\bar{1}02$: $\bar{1}00$	5	73 0 — 73 43	73 15	73 20
100 : 122	23	80 54 — 81 17	81 9	—
122 : $\bar{1}00$	23	98 41 — 99 2	98 51	98 51
100 : 322	2	65 44 — 66 1	65 52½	65 54
322 : 122	2	15 12 — 15 16	15 14	15 15
122 : $\bar{1}2\bar{2}$	12	56 30 — 56 54	56 43	—
$\bar{1}2\bar{2}$: $1\bar{2}2$	12	122 58 — 123 27	123 17	123 17
101 : 110	4	79 49 — 80 10	80 0	80 6
110 : $\bar{1}0\bar{1}$	4	99 49 — 100 10	100 0	99 54
101 : 122	4	62 35 — 62 48	62 42	62 39
122 : $\bar{1}0\bar{1}$	4	117 12 — 117 27	117 16	117 21
100 : 110	4	71 42 — 71 54	71 49	71 52
110 : $\bar{1}10$	2	36 19 — 36 27	36 23	36 16

Zinc p-dichlorobenzenesulphonate, $Zn(C_6H_3Cl_2SO_3)_2.8H_2O$.—This salt crystallises in groups of long prisms when a hot solution is allowed to cool or in single short prisms when a cold saturated solution is allowed to evaporate. The crystals are always slightly distorted, opposite faces not being quite parallel. The most prominent form developed is a\{100\}, the other forms on the prism zone being q\{101\}, e\{$\bar{1}$01\}, p\{$\bar{3}$01\}; this zone is striated and no angles measured in the zone were used in calculating the axial ratios. The faces forming the prism ends were beautifully developed, the forms being r\{111\}, t\{012\}, s\{111\}. No definite cleavage could be detected (see fig. 9).

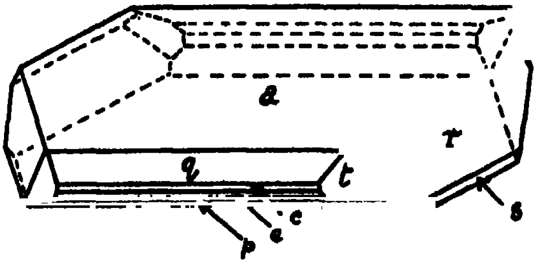

Fig. 9.—$Zn(C_6H_3Cl_2SO_3)_2.8H_2O$.

Water: found 22·42 per cent.; $(C_6H_3Cl_2SO_3)_2.Zn.8H_2O$ requires 21·77 per cent.

Zinc: found 9·89 per cent.; calculated 9·88 per cent.

System: Monosymmetric.

Axial ratios: $a:b:c = 2{\cdot}9985:1:2{\cdot}4539$. $\beta = 79° 20'$.

Angle.	No. of observations.	Limits.	Mean observed.	Calculated.
101 : 111	15	59° 44′—59° 51′	59° 47′	—
101 : $\bar{1}$11	7	60 20 —60 29	60 26	60° 26′
001 : 012	15	50 18 —50 27	50 20	—
012 : 01$\bar{2}$	7	79 14 —79 23	79 19	79 20
001 : 111	12	65 30 —65 42	65 38	—
111 : 11$\bar{1}$	8	42 45 —43 1	42 51	42 49
11$\bar{1}$: 00$\bar{1}$	7	71 23 —71 37	71 31	71 33
100 : 111	6	68 52 —69 0	68 57	68 56
111 : $\bar{1}$11	4	34 40 —34 44	34 42	34 44
$\bar{1}$11 : 00$\bar{1}$	4	76 19 —76 24	76 21	76 20
$\bar{1}$01 : $\bar{1}$11	2	64 9 —64 12	64 10½	64 8
100 : 101	14	44 30 —44 53	44 40	44 24
101 : 001	11	34 33 —34 52	34 41	34 56
100 : 001	12	79 16 —79 29	79 23	79 20
001 : $\bar{1}$01	8	43 28 —43 34	43 31	43 28
$\bar{1}$01 : $\bar{3}$01	3	33 41 —33 48	33 45	33 47
001 : $\bar{3}$01	12	77 14 —77 23	77 18	77 15
$\bar{3}$01 : $\bar{1}$00	16	23 16 —23 25	25 19	23 25

Magnesium p-dichlorobenzenesulphonate, $(C_6H_3Cl_2SO_3)_2Mg.8H_2O$.—Well-developed crystals of this salt were obtained in the form of fairly stout plates or short prisms by allowing an aqueous solution to evaporate slowly at 25° C. The angular measurements of the crystals are almost identical with those of the zinc salt. The crystals belong to the hemimorphic class of the monosymmetric system, as they are destitute of a plane of symmetry, the two ends of the prisms (which are elongated in the direction of the *b* axis) being differently developed. The form $\{\bar{2}\bar{1}2\}$ invariably appears on only one end of the prism, being sometimes so largely developed at that end that other forms are almost entirely suppressed. The prisms appear to consist of two individuals imperfectly twinned on {010}, and to be expanded in a belt around the middle of the prism; moreover, the faces on opposite ends of the prism are never truly parallel.

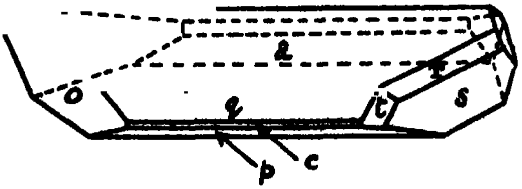

Fig. 10.—$Mg(C_6H_3Cl_2SO_3)_2.8H_2O$

The forms developed are the same as those obtained in the case of the zinc salt, together with the hemimorphic form $\{\bar{2}\bar{1}2\}$. The habit is slightly different from that of the zinc salt, as a comparison of the two figures will show. The prism zone is badly striated parallel to the *b* axis. No definite cleavage was detected (see fig. 10).

Water: found 22·66; calculated 23·23 per cent.

System: Monosymmetric hemimorphic.

Axial ratios: $a : b : c = 2{\cdot}9970 : 1 : 2{\cdot}4450$. $\beta = 79° 41\frac{1}{2}'$.

Angle.	No. of observations.	Limits.	Mean observed.	Calculated.
$101 : 111$	15	59° 45′—59° 54′	59° 49′	—
$111 : \bar{1}1\bar{1}$	8	60 16—60 26	60 23	60° 22′
$\bar{1}11 : 11\bar{1}$	12	51 41—52 19	51 57	—
$100 : 111$	9	68 46—69 17	69 2	69 3
$111 : \bar{1}11$	16	34 31—34 48	34 43	—
$\bar{1}11 : \bar{1}00$	11	76 5—76 24	76 14	76 14
$001 : 111$	1	——	65 35	65 41
$111 : 11\bar{1}$	7	42 50—43 6	42 57	42 56
$11\bar{1} : 00\bar{1}$	2	71 19—71 29	71 24	71 23
$\bar{1}00 : \bar{2}\bar{1}2$	4	67 34—67 52	67 47	67 43
$\bar{2}\bar{1}2 : 0\bar{1}2$	2	——	28 58	28 52
$0\bar{1}2 : 100$	2	83 12—83 22	83 17	83 25
$001 : 012$	4	50 16—50 22	50 19	50 15½
$\bar{2}\bar{1}2 : \bar{1}11$	4	18 2—18 10	18 6	18 16

The values are summarised in the following table:—

Salt.	W.	Axial ratios. *a* : *b* : *c*.	β.	Fractions used.	Equivalence parameters.* *x* : *y* : *z*.
$(C_6H_5SO_3)_2Zn.6H_2O$	100	3·546 : 1 : 1·108	86° 6′	4*c*/3	9·4844 : 3·9518 : 2·6747
$(C_6H_5SO_3)_2Mn.6H_2O$	100	3·602 : 1 : 1·1142	86 24½	4*c*/3	9·5640 : 3·9448 : 2·6552
$(C_6H_5SO_3)_2Mg.6H_2O$	100	3·538 : 1 : 1·1099	86 38	4*c*/3	9·4940 : 3·9321 : 2·6834
$(C_6H_5SO_3)_2Cd.6H_2O$	100	3·645 : 1 : 1·123	86 20½	4*c*/3	9·6160 : 3·9600 : 2·6381
$(C_6H_5SO_3)_2Cu.6H_2O$	100	3·653 : 1 : 1·114	86 38	4*c*/3	9·6547 : 3·9257 : 2·6430
$(C_6H_4CH_3.SO_3)_2Zn.6H_2O$	112	4·020 : 1 : 1·1081	88 26	4*c*/3	10·709 : 3·9266 : 2·6637
$(C_6H_4CH_3.SO_3)_2Mn.6H_2O$	112	4·078 : 1 : 1·1181	88 18½	4*c*/3	10·7882 : 3·9261 : 2·6454
$(C_6H_4CH_3.SO_3)_2Mg.6H_2O$	112	4·035 : 1 : 1·1055	88 27½	4*c*/3	10·7362 : 3·9220 : 2·6606
$(C_6H_3Cl_2SO_3)_2Zn.8H_2O$ ...	108	2·4539 : 1 : 2·9985	79 20	3*a*/2, *c*/2	9·9770 : 4·0637 : 2·7106
$(C_6H_3Cl_2SO_3)_2Mg.8H_2O$ ...	108	2·4450 : 1 : 2·9970	79 41½	3*a*/2, *c*/2	9·9507 : 4·0658 : 2·7132
$(C_6H_4CH_3SO_3)NH_4$.........	50	0·8922 : 1 : 1·4505	90 0	3*a*/2, *c*/2	5·1030 : 3·6758 : 2·6656
$(C_6H_4CH_3SO_3)K.H_2O$......	48	0·8650 : 1 : 3·2982	90 0	2*a*, *c*/4	3·2285 : 5·5854 : 2·6618
$(C_6H_4CH_3SO_3)Ag$	44	1·4339 : 1 : 2·5286	87 14½	*c*/3	3·3168 : 4·7520 : 2·7957
$(C_6H_3Cl_2SO_3)Na.H_2O$	42	1·9583 : 1 : 3·0529	88 46	2*a*/3, *c*/4	4·5650 : 3·4965 : 2·6563
$(C_6H_3Cl_2SO_3)K$	38	0·7636 : 1 : 1·5064	83 27½	3*a*/2, *c*/2	4·0548 : 3·5401 : 2·6646
$C_6H_3Cl_2SO_3H.3H_2O$	50	0·2918 : 1 : 0·6255	79 36	2*a*, 3*c*/4	3·3296 : 5·7050 : 2·6763
or	150	0·2918 : 1 : 0·6255	79 36	2*a*, 3*c*/4	9·9888 : 5·7050 : 2·6763

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* The choice of symbols for the parameters being arbitrary, the values have been arranged so as to bring them into harmony and are not always in the order corresponding to the axial ratios.

A glance at the column of equivalence parameters shows that, throughout the series, with one exception, one parameter has a practically constant value, as it varies only between 2·64 and 2·68, the mean value being 2·658. This value has been met with in all the salts of tervalent metals previously discussed and must be taken to represent the distance between corresponding points in successive layers of benzene complexes in rhombohedral marshalling. The occurrence of this value is proof that in the crystalline structure of all the salts considered, as in those of tervalent metals, the substituting groups are not intruded *between* the layers of benzene complexes but are included *within* and form part of these layers.

In view of the conclusion that the crystalline form of *p*-dichlorobenzenesulphonic acid is similar to that assumed by salts of tervalent metals and that its molecules become grouped in triads, it is important to consider whether there be any evidence of such an arrangement in the case of the salts of monad metals. In only one instance, that of potassium *p*-toluenesulphonate, does this appear to be immediately obvious. The axial ratio $a:b$ in this salt is 0·865 : 1, a value almost identical with the ideal trigonal ratio 0·866 : 1. It will be noticed that the parameter values of this salt are very similar to those of dichlorobenzenesulphonic acid and that the two compounds have nearly the same valency volume. It is further legitimate to assume that as the value 2·6618 represents the thickness of each layer, the z value (3·2285) is that in the direction DO in fig. 6, the y value (5·8855) being that of AD.

In silver toluene-*p*-sulphonate one parameter has the value 2·7957, which is practically that of the z parameter of the second form of benzene, 2·780. It is highly probable, therefore, that the crystal structure of this compound is modelled on the hexagonal type of benzene marshalling, not the rhombohedral. It has been pointed out already that the two modes of arrangement differ essentially only in the manner in which successive layers of benzene complexes are packed together one upon the other.

It is conceivable that the trigonal arrangement prevails also in this salt and that it differs merely in being derived from "hexagonal" rather than "rhombohedral benzene." Further, it may be regarded as not improbable that the remaining salts of the group are similarly constituted, though the evidence is of such a character that no definite conclusion is possible at present.

Though the equivalence parameters of the rhombohedral type of benzene are not known, they are probably numerically very close to those of *p*-diiodobenzene. The equivalence parameters of this substance are

$$x:y:z = 3{\cdot}1402:3{\cdot}6161:2{\cdot}6419.$$

When one hydrogen atom is displaced by the sulphonic group, it is to be expected that a considerable elongation will be produced in one direction in the crystal structure, that is to say, in the direction either of the x or of the y parameter; it may also be anticipated that the adjustments necessary to bring the assemblage into a close-packed condition would involve a certain amount of distortion which would affect the dimension of the other parameter. The introduction of molecules of water of crystallisation would also produce a dimensional change, probably an elongation in the same direction as that affected by the sulphonic group; a methyl group in the p-position might be expected to produce an elongation in the same direction. Finally, it is to be supposed that one parameter in each of the salts would correspond more or less closely with either the x or the y value of rhombohedral benzene, *i.e.* with 3·140 or 3·616; the other should be considerably greater.

It is noteworthy, therefore, that in the three salts under consideration the y parameter approaches as closely as can be expected to the y value, 3·616, of p-diiodobenzene, the third parameter being considerably elongated and varying according to the nature of the compound.

	Equivalence parameters.		
Salt	x	y	z
$C_6H_3Cl_2SO_3Na.H_2O$	4·5650 :	3·4965 :	2·6563
$C_6H_3Cl_2SO_3.K$	4·0548 :	3·5401 :	2·6646
$C_6H_4CH_3SO_3.NH_4$	5·1030 :	3·6758 :	2·6656

As the argument adopted in the previous communication and also in the present has been that there is close analogy in structure between p-diiodobenzene and the sulphonates of pseudo-trigonal form, this close correspondence between the salts of the monad metals and the diiodo-compound might be regarded as an indication that these latter salts are also of pseudo-trigonal form. If this point of view be accepted, the y values should be trebled and, therefore, are not to be compared with those of the salts of bivalent metals.

A second possibility, however, is that in some cases the structure of the salts of monad metals is similar to that which appears to be characteristic of those of dyad metals now to be discussed, two atoms of the monad metal taking the place of the dyad. Probably such questions as these will be settled only by the study of the optical properties of the salts or by the application of methods such as are now being developed involving the use of X-rays.

Passing to the salts of bivalent metals, the marked elongation of the x parameter is the striking feature (see table, p. 307). It is scarcely possible to doubt that the influence of the metallic atoms is exercised from a mean position between two "lines" of benzene molecules which become thrust apart by the intrusion of the sulphonic radicles connected in pairs with the metallic atoms and the attendant molecules of water. This mode of arrangement is represented in fig. 11, which is drawn to scale in the manner already explained.

On contrasting the parameter values with the dimensions of the full-line figure, which is constructed from the assumed parameter values of rhombohedral benzene and the valency volume of the salt, it appears that whilst slight compression is exercised in one direction (that of x) there is a corresponding expansion in the direction at right angles to x.

This alteration, which is shown by the broken line figure, corresponds to that involved in the case of trigonal salts in the compression of the irregular figure into the triangular form. It may be taken to represent the orienting influence exercised at and from the centre of the metallic atom.

It appears to be a noteworthy point that whereas in the case of the salts of triad and monad metals a perfect cleavage plane exists in the plane of the layers of benzene, no such cleavage is manifest in salts of the dyad metals. On reference to fig. 6, it is noticeable that whereas, in the case of the triad metallic salts, the three hydrogen atoms displaced are in one plane, the two atoms displaced by the salts of the dyad metal are in different planes.

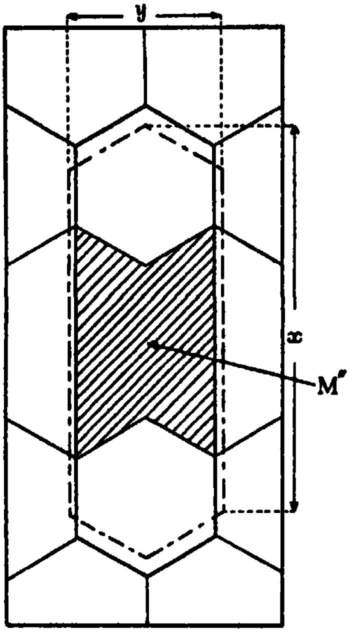

Fig. 11.

Obviously if the atoms thus displaced were those belonging to different benzene molecules in two superposed layers, the benzene layers would be tied together and it is not only conceivable but to be expected that in such a case there would be no cleavage plane.

The present inquiry has shown that in selecting for study paradibromobenzenesulphonic acid and the rare earths a peculiarly fortunate choice was made, as attempts to use other acids and other oxides of tervalent metals have been attended with but little success. The acids used unsuccessfully include *p*-diiodobenzenesulphonic, *p*-bromobenzenesulphonic, 1·3-dibromobenzene-4-sulphonic, 1·3-dibromobenzene-5-sulphonic, *m*-nitrobenzenesulphonic and *m*- and *p*-benzenedisulphonic acids. The salts derived from *p*-diiodobenzenesulphonic acid are noteworthy on account of their slight solubility in water; they crystallise in thin flakes unsuitable for goniometric measurement. The following figures show how much less soluble the salts of the diiodo-acid are than those of the dibromo-acid:—

Salt.	Anhydrous salt dissolved per 100 grm. water at 25·1° C.
$La(C_6H_3Br_2SO_3)_3.9H_2O$	4·52 grm.
$Nd(C_6H_3Br_2SO_3)_3.9H_2O$	6·81 „
$Nd(C_6H_3I_2SO_3)_3.10H_2O$	1·21 „

Of the salts of the other acids used, none crystallised well from water, most of them being very soluble; nor were better results obtained when either alcohol or ethylic acetate or mixtures of these with water were used as solvents.

In the hope of gaining information which would be of service in determining the position of the rare earths in the periodic scheme of classification, the ferric, chromium and aluminium salts of *p*-dibromobenzenesulphonic acid were studied; unfortunately, these all crystallise with much water in masses of very fine needles and have not been obtained in measurable form. The normal ferric salt, a white compound, is stable only in presence of an excess of acid: water readily hydrolyses it into a yellow basic salt, $Fe(OH)(C_6H_3Br_2SO_3)_2.12H_2O$; this is further decomposed by water in neutral solution and converted into a more basic salt the composition of which has not been determined.

Although it has not therefore been possible to establish any morphotropic relationship between the salts of the rare earth metals and those of other tervalent metals, yet it is extremely probable that some such relationship does exist. In this connexion, it is interesting to note that Bodman* has shown that the nitrates of didymium and bismuth are isodimorphous and crystallise together.

The p-Dibromobenzenesulphonates of Iron, Chromium and Aluminium.

The following is a brief account of these salts, which have not hitherto been described. In each case the salt was prepared by dissolving the hydroxide of the metal, purified by dialysis, in a solution of the sulphonic acid.

Ferric p-dibromobenzenesulphonate.—Ferric hydroxide dissolves only to a limited extent in *p*-dibromobenzenesulphonic acid. The solution so obtained is dark yellow when hot but colourless when cold; it deposits the normal ferric salt in the form of a mass of very fine white needles. This salt cannot be recrystallised from water, since it is stable only in presence of excess of acid. For analysis it was filtered from the solution, washed with cold water and dried on a porous plate; on standing, it gradually became yellow, owing to loss of water. The ratio of metal to acid radicle was determined by dissolving the salt in cold water, precipitating the iron with ammonia and weighing as Fe_2O_3, the amount of ammonium *p*-dibromobenzenesulphonate left in solution being determined by evaporating to dryness and weighing. The mean of two determinations gave

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* 'Ber.,' vol. 31, p. 1237.

$$Fe : (C_6H_3Br_2SO_3) = 1 : 2{\cdot}985.$$

The results obtained for the sample analysed agreed with the formula $Fe(C_6H_3Br_2SO_3)_3.13H_2O$ but it is doubtful whether this be the true formula.

	Fe	$(C_6H_3Br_2SO_3)$	H_2O
Calculated	4·53 per cent.	76·52 per cent.	18·95 per cent.
Found	4·55 „	76·39 „	19·69 „

The salt dissolves readily in alcohol and ether giving yellow solutions.

Basic Ferric p-dibromobenzenesulphonate.—When the normal salt is dissolved in warm water and the solution is allowed to cool, a basic salt separates in the form of golden yellow spangles. This salt is itself decomposed by warm water giving a brick-red coloured precipitate which has not been analysed. The analytical figures for the yellow salt agree with the formula $Fe(OH)(C_6H_3Br_2SO_3)_2.12H_2O$.

	Fe	H_2O
Calculated	6·05 per cent.	23·50 per cent.
Found..............	6·06 „	23·92 „

Chromium p-dibromobenzenesulphonate.—This salt crystallises from aqueous solution in masses of fine bluish needles, very soluble in water, giving a dichroic solution. It is soluble also in alcohol and ether. The analytical results agree with the formula $Cr(C_6H_3Br_2SO_3)_3.14H_2O$.

Ratio $Cr : (C_6H_3Br_2SO_3) = 1 : 2{\cdot}86$.

	Cr	$(C_6H_3Br_2SO_3)$	H_2O
Calculated	4·21 per cent.	75·62 per cent.	20·17 per cent.
Found	4·42 „	75·60 „	19·87 „

Aluminium p-dibromobenzenesulphonate.—This salt crystallises in masses of fine white needles from aqueous solution. It is easily soluble in water and in alcohol and ether. Analytical results agree with the formula $Al(C_6H_3Br_2SO_3)_3.18H_2O$.

Ratio $Al : (C_6H_3Br_2SO_3)$ found $= 1 : 3{\cdot}00$.

	Al	$(C_6H_3Br_2SO_3)$	H_2O
Calculated	2·09 per cent.	72·91 per cent.	25·0 per cent.
Found..............	2·10 „	73·50 „	24·0 „

Scandium p-dibromobenzenesulphonate.—This salt crystallises from aqueous solution in colourless, long, thin striated plates belonging to the monosymmetric system. Analysis agrees with the formula $Sc(C_6H_3Br_2SO_3)_3.14H_2O$.

Water: found 20·30; calculated 20·30 per cent.

Cobaltous p-dibromobenzenesulphonate.—The salt was obtained in an attempt to prepare the cobaltic salt by neutralising the acid with cobaltic oxide; it crystallises in long thin pink needles. Analysis agrees with the formula $Co(C_6H_3Br_2SO_3)_2 . 9H_2O$.

Water: found 18·96; calculated 19·04 per cent.

Cobalt in anhydrous salt: found 8·57; calculated 8·56 per cent.

Summary.

The present account is an extension of the previous communication in which it was shown that the *p*-dibromobenzenesulphonates of several of the tervalent rare-earth metals all crystallise in pseudo-trigonal forms. In the light of the Barlow-Pope hypothesis these are to be regarded as so constituted that the molecules are arranged in layers in a plane at right angles to the pseudo-trigonal axis.

Each such layer appears to be of the thickness attributed to a single layer of benzene molecules in crystalline benzene or one of its halogen derivatives.

In the formation of the sulphonate the benzene structure is opened out to admit of the introduction of the sulphonic radicles, of the metallic atoms and of water molecules between the benzene molecules in such manner that the trigonal symmetry of the original structure is either preserved or at most only slightly modified.

It is now shown that similar conclusions may be drawn with reference to the structure of *p*-dichlorobenzenesulphonic acid, several salts of which isomorphous with *p*-dibromobenzenesulphonates are described.

The structure of sulphonates containing monad and dyad metals is also discussed. It is argued that in the formation of the latter the molecules of benzene in contiguous rows become separated by the intervention of the sulphonic radicles (together with water) which are united in pairs by the metallic atom.

The structure of the salts containing monad metals appears in some cases to be pseudo-trigonal like that of the acid; in others to resemble that of salts of dyad metals.

Diagrams to scale are given illustrating the molecular structure of the several types of crystal.

It is proposed to study the optical properties of crystals of salts such as those described, in the hope of discovering criteria significant of the several types.

The Energy of Röntgen Rays.[*]

By R. T. BEATTY, M.A., D.Sc., Emmanuel College, Clerk Maxwell Student of the University, Cambridge.

(Communicated by Prof. Sir J. J. Thomson, F.R.S. Received June 10,—Read June 26, 1913.)

In this paper an account will be given of experiments which have been made to determine the amount of energy which reappears as Röntgen radiation when homogeneous cathode rays of given speed fall upon anticathodes of different materials.

The method of attack is modified from that used in a previous research on "The Direct Production of Röntgen Radiations by Cathode Particles."[†] Fig. 1 is taken from that paper, and shows how cathode rays of given speed, which have been isolated by means of magnetic deflection, strike an anticathode situated in the tube A. The Röntgen rays so produced pass into an ionisation vessel B, and the ionisation due to them is measured by an electroscope C.

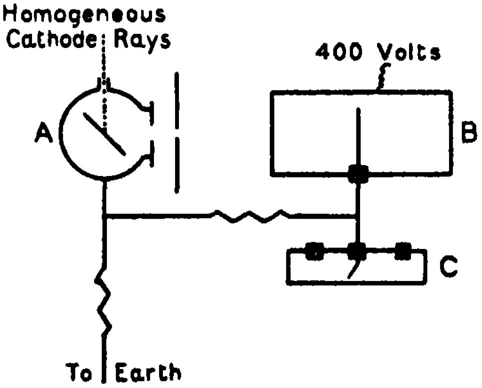

FIG. 1.

Now, in order to absorb the Röntgen rays completely, and so measure their total energy of ionisation, a long zinc cylinder was made, 150 cm. long and 10 cm. in diameter. A calculation of the absorption coefficients of various substances for Röntgen rays showed that, if this cylinder were filled with air which had been saturated with the vapour of methyl iodide (CH_3I) at room temperature, then total absorption of the Röntgen rays should take place if the rays were generated by cathode rays whose velocity did not exceed 8×10^9 cm. per second.

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[*] The expenses of this research have been partly covered by a Government Grant from the Royal Society.

[†] Beatty, 'Roy. Soc. Proc.,' A, vol. 87. pp. 511–518.

In the next place, it was thought desirable that the thin window through which the Röntgen rays escape from the vacuum chamber into the ionisation chamber should be so thin that the absorption of the Röntgen rays by it could be neglected. This is an essential point, because even homogeneous cathode rays, on striking an anticathode, become heterogeneous as they penetrate into the anticathode, and so give rise to heterogeneous Röntgen rays. We know the absorption coefficients of most of the common elements for homogeneous Röntgen rays, but evidently cannot apply these values to the heterogeneous Röntgen rays now under discussion.

To produce the thin window, a lead plate 1 mm. thick was pierced with a number of fine holes, each about 1/30 mm. diameter, the holes all lying within a circle of 1·5 mm. diameter. This was accomplished by placing the lead plate on a plate of glass and making the holes with a very fine needle; the lead plate was then covered with aluminium leaf 0·002 mm. thick, which was stuck on with shellac, and in this way a window was produced, which would stand a difference of pressure of an atmosphere on the two sides, and whose maximum absorption of the rays which were used did not exceed 1 per cent.

In fig. 2 the ionisation chamber is shown placed in position. A cone of rays has been represented as starting from the illuminated portion of the anticathode, passing through the window, and diverging along the chamber.

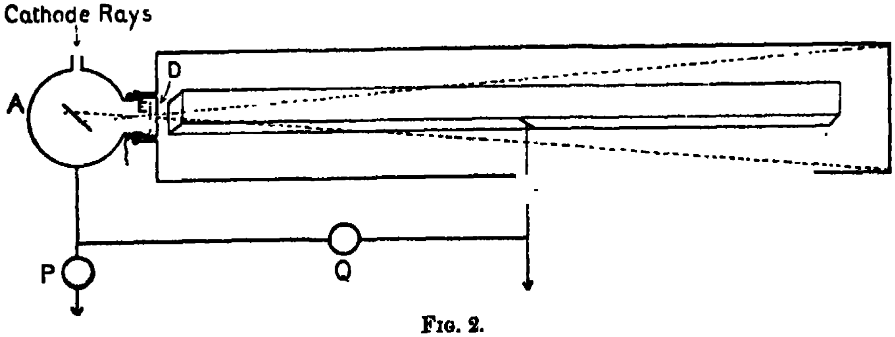

Fig. 2.

Obviously, the actual cone of X-rays must lie inside this one if the rays are to be totally absorbed without striking the curved surface of the cylinder.

The axis of the beam of rays was found by a photographic method, and the cylinder correspondingly aligned. The cylinder was then waxed on to the end of the vacuum tube, as shown in fig. 2, and air saturated with the vapour of methyl iodide was drawn into it.

From fig. 3 it will be seen that, on plotting the ionisation caused by the Röntgen rays against the sixth power of the velocity of the cathode rays, straight lines are obtained, until the velocity of the cathode rays exceeds $8{\cdot}25 \times 10^9$ cm. per second. The abruptness of the change led me to suspect that the rays were not totally absorbed when this velocity was exceeded.

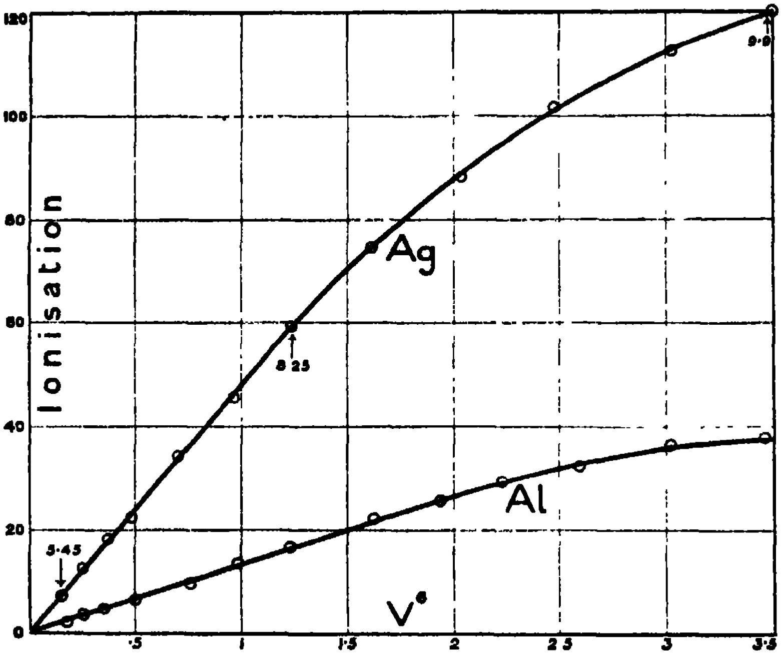

Fig. 3.

To test this, the zinc cylinder was replaced by one of brass, which was strong enough to be exhausted. Methyl iodide was admitted at almost saturation pressure.

The curves (fig. 4) now become straight lines within the limits of velocities used, showing that, as suspected, total absorption had not been obtained with the former apparatus. A number of experimental errors have, however, still to be discussed, and it will be shown that the real relation is quite different from that shown in fig. 4.

These preliminary results having been obtained, a more detailed investigation was now made of possible experimental errors.

Elimination of Experimental Errors.

In the first place, the method of averaging a galvanometer deflection over the space of a minute is unsatisfactory with such a fluctuating current as is given by a discharge tube. Frequently, out of ten attempts to take a reading, only one is obtained with a sufficiently steady reading of the galvanometer.

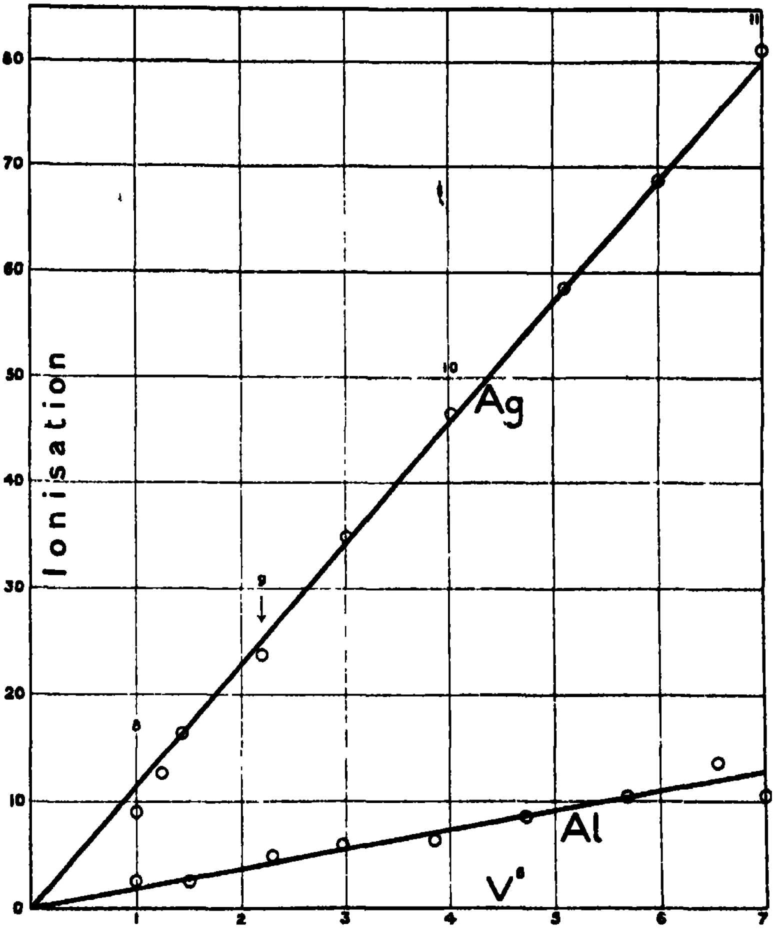

Fig. 4.

This unsteadiness of the tube is, indeed, the greatest difficulty met with in work of this kind.

In a previous paper on "The Direct Production of Characteristic Röntgen Radiations" (*loc. cit.*), a balancing method was used, in which the readings depended only on the ratio of two resistances P and Q, the electroscope being used as a null instrument. One of these resistances was composed of a mixture of copper sulphate and glycerine, the other of xylol and absolute alcohol.

It was determined to use a similar method in the present experiment, but to employ metallic resistances.

These resistances will be but briefly described here, as a complete description of them will form the subject of a separate paper. They were made by depositing films of platinum *in vacuo* upon quartz rods until the required conductivity was obtained. The necessary metallic connections were sealed in the surrounding evacuated glass tube and soldered to the ends of the quartz rod.

The behaviour of these films is a function of their thickness. They are quite unstable when the resistance lies between 10^8 and 10^{10} ohms; for smaller resistances they become more constant, while for resistances greater than 10^{10} ohms they acquire perfect stability in a few weeks; in the resistances of this order which were finally selected for use Ohm's Law was found to be obeyed.

A platinum resistance of this kind was now used for Q (fig. 2), its resistance was $5{\cdot}57 \times 10^{10}$ ohms; a laboratory megohm was used for P.

In the preliminary experiments, approximate saturation of the ionisation current had been obtained with a central rod electrode when the cylinder was kept at a potential of 400 volts. To obtain complete saturation more drastic methods were now found necessary. A rectangular framework of copper gauze, 6 cm. × 3 cm. in cross-section and 1 metre in length, was used as electrode, and inside this a gauze strip 3 cm. broad was tightly stretched, so that when the outer brass cylinder and the gauze strip were kept at 400 volts the potential gradient never fell below 260 volts per centimetre anywhere in the region where ionisation took place. Fig. 5 shows the saturation curve so obtained with different pressures of methyl iodide. There was still a possibility that since the tube D (fig. 2) was at a potential of 400 volts, it might act as anode to the vacuum tube when the discharge was running, and so give a wrong value to the cathode ray current.

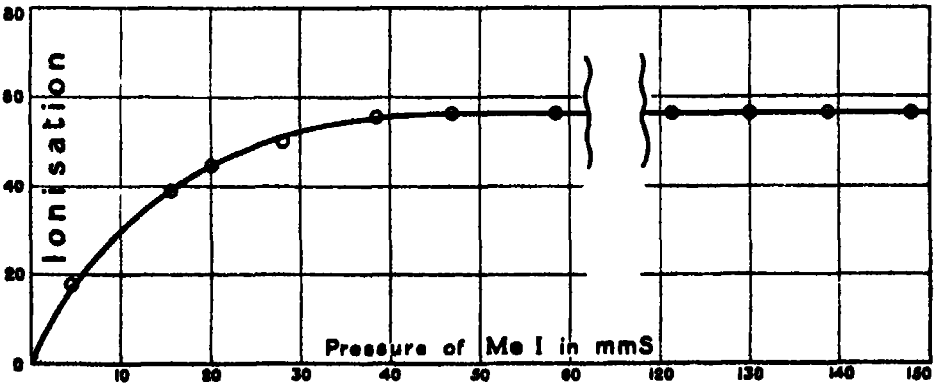

Fig. 5.

The tube D had been lined inside with shellac to obviate such an occurrence but it was thought that discharge might take place from the aluminium window, 1 mm. diameter, which, of course, could not be covered with shellac. An earthed ring electrode was accordingly placed at E, so as to prevent such discharge reaching the lining of the tube A. Then the discharge tube was started, using cathode rays of given speed, and the ionisation in the long cylinder due to the Röntgen rays was measured for different voltages applied to the cylinder. The cylinder in this experiment contained air at a pressure of 10 cm., so that saturation could be obtained at much lower voltages than 400 volts. Hence any deviation from the usual form of saturation curve was to be attributed to a subsidiary discharge in the vacuum tube, due to the air insulation breaking down under the voltage applied to the tube D.

Table I shows the values of the resistance P necessary to balance the electroscope when cathode rays of speed from 7×10^9 to 9×10^9 cm./sec. were used. P would, in the ordinary way, be proportional to the ionisation in the long cylinder per unit cathode ray current, and, if saturation were obtained, would be constant, in spite of altering the voltage applied to the long cylinder. Now, from fig. 5 we see that saturation actually is attained under these conditions. Hence any change in P as the voltage is altered would indicate a disturbed value for the cathode ray current, due to a subsidiary discharge which might be expected to increase with the voltage applied. From Table I we must conclude that no abnormal effect comes in till the pressure in the vacuum tube is such that cathode rays of speed 9×10^9 cm./sec. are produced.

Table I.

T+10³.					Voltage on cylinder.
V+10⁹ ... 7.	7·5.	8.	8·5.	9.	
20	27	37	51	73	400
20	27	37	51	75	350
20	27	37	51	75	300
20	27	37	51	70	200
20	27	37	51	70	100
20	27	37	51	69	50
20	27	37	51	68	20

Let us now review the progress that has been made in eliminating experimental errors. We have placed the long cylinder properly in alignment, and have shown that the Röntgen rays cannot strike the curved surface of this cylinder and that they are totally absorbed by the gas inside. We have obtained complete saturation of the ionisation current, and we have shown that no subsidiary or false discharge occurs till the speed of the cathode rays rises to 9×10^9 cm./sec.

The method of balancing the electroscope readings requires that the platinum resistance Q should keep constant and obey Ohm's law. Only a brief mention of its behaviour has been made in this paper, but in a later contribution it will be shown that these conditions were fulfilled in the resistances which were selected for use.

Effect of Reflected Cathode Rays.

But there is an additional possibility of error which at first sight appeared formidable. When cathode rays strike an anticathode some of them are turned back and do not complete their path in the anticathode. Now if a considerable amount of the energy (not necessarily the number) of the cathode rays is diverted in this way a correction must be made in our results. But the whole subject of scattering of cathode rays of speeds ranging from 6×10^9 to 10^{10} cm./sec. has never been studied quantitatively. Measurements have only been made for β-rays,* where in some cases 70 per cent. of the incident beam has been found to be reflected, and for cathode rays of speeds of 1000 volts or less,† where no reflected rays of speed greater than 25 volts have been found.‡

One might, as Sir J. J. Thomson suggested to me, make the anticathode of metal leaf in the form of a Faraday cylinder so as to catch all the cathode rays. Such a cylinder, however, would have subtended so large an angle at the window that the emergent cone of rays would have struck the wall of the ionisation cylinder before being completely absorbed by the gas inside.

Evidently the Faraday cylinder must be made extremely small. Now a surface of soot or platinum black may be considered as an aggregate of imperfectly formed Faraday cylinders and it might be expected that less reflection would be obtained from such surfaces than from the polished material.

To test this point the ionisation cylinder and the window were removed and a brass tube furnished with two diaphragms and a Faraday cylinder was substituted (fig. 6). The number of reflected cathode rays entering this cylinder was determined as a fraction of the number of primary rays incident on the anticathode. Then knowing the solid angle of the cone of reflected rays entering the Faraday cylinder we can calculate the percentage of rays reflected in all directions.

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* Kovarik, 'Phil. Mag.,' Nov. 1910, vol. 30, pp. 849–866.

† Lenard, 'Ann. d. Phys.,' 1904, vol. 15, p. 485; Von Baeyer, 'Verh. D. P. Ges.,' 1908, vol. 10, pp. 96, 953; Gehrts, 'Ann. d. Phys.,' Dec. 21, 1911, vol. 15, p. 995.

‡ The term "cathode ray of speed of *n* volts" means an electron whose speed is that which would be acquired by falling through a potential difference of *n* volts.

A small bar magnet was then brought close to the Faraday cylinder so that only the faster reflected rays could reach this cylinder.

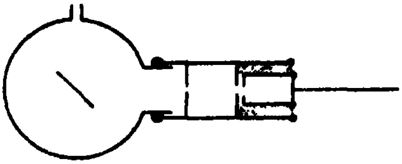

Fig. 6.

The results are shown in Table II. Column 4 contains the numbers in Column 3 expressed as percentages of those in Column 2.

Table II.

Radiator.	Reflected rays as percentage of incident rays.		Percentage escaping magnetic field.
	Magnet off.	Magnet on.	
Graphite	60	12·0	20·0
Soot	46	3·8	8·25
Platinum	87	35·0	40·2
Platinum black	73	9·0	12·3

It thus appears that soot only reflects about two-fifths of the fast rays compared with graphite, while from platinum black the fast rays are only 30 per cent. of those from polished platinum. Hence these porous materials when used as anticathodes should give a closer approximation to the true form of the curve for the energy of the X-rays than should graphite or polished platinum.

The ionisation cylinder was next put in position again and filled with methyl iodide vapour.

For different speeds of cathode rays the ionisation due to the Röntgen rays was determined for four anticathodes. On comparing the curves it was found that the results for platinum and platinum black were identical, as also those for graphite and soot.

This remarkable result shows at once that the reflected cathode rays must carry only a few per cent. of the energy of the incident cathode rays, as otherwise the energies of the emitted Röntgen rays would not be identical for the anticathodes when polished and when finely subdivided.

As no further source of experimental error now appeared probable the final step was taken of comparing the ionisation energy of the Röntgen rays from an anticathode with the energy of the cathode rays incident upon that anticathode.

The Final Experiments.

Results have been obtained with anticathodes of rhodium, silver, and aluminium, and preliminary curves have been obtained for copper.

As the numerical results have been calculated from the curve obtained for rhodium a few remarks may be made about the behaviour of this anticathode. It is not easily oxidised, so that one may be sure that the cathode rays are not absorbed in a film of oxide. Again we can obtain two characteristic radiations from rhodium. One is to be expected when the speed of the cathode rays exceeds $2{\cdot}6 \times 10^9$ cm./sec., but it is very easily absorbed and carries but little energy. The other is known to occur when the speed of the cathode rays exceeds 10^{10} cm./sec. This speed was not reached in the experiments and so the second characteristic radiation did not appear.

In fig. 7 are given the relative ionisations due to the Röntgen rays per unit cathode ray when cathode rays of different speeds are used. The curves for silver and aluminium are the mean of four sets of readings; for rhodium eight sets were taken, while the curve for copper is merely a preliminary result.

It will be seen that when characteristic radiations are not excited the energy of the Röntgen rays is proportional to the fourth power of the velocity of the parent cathode rays.

With copper the same result holds good till the rays exceed a speed of $6{\cdot}25 \times 10^9$ cm./sec.; then the line bends abruptly owing to the presence of the characteristic radiation.

We now proceed to calculate the absolute values. From fig. 7 we see that when $V = 10^{10}$ cm./sec. the balancing resistance P must be 82,400 ohms for a rhodium anticathode. Now the resistance Q was $5{\cdot}57 \times 10^{10}$ ohms. Hence

$$\frac{\text{Ionisation current due to X-ray pencil}}{\text{Cathode ray current}} = \frac{82400}{5{\cdot}57 \times 10^{10}} = 1{\cdot}48 \times 10^{-6}.$$

The diameter of the thin window = 0·0392 cm.
Distance of window from anticathode = 6·94 „

Therefore

$$\frac{\text{Solid angle of X-ray pencil}}{4\pi} = \frac{\pi(0{\cdot}0196)^2}{(6{\cdot}94)^2 4\pi} = 1{\cdot}99 \times 10^{-6}.$$

Hence if we assume that the X-rays are emitted uniformly in all directions,

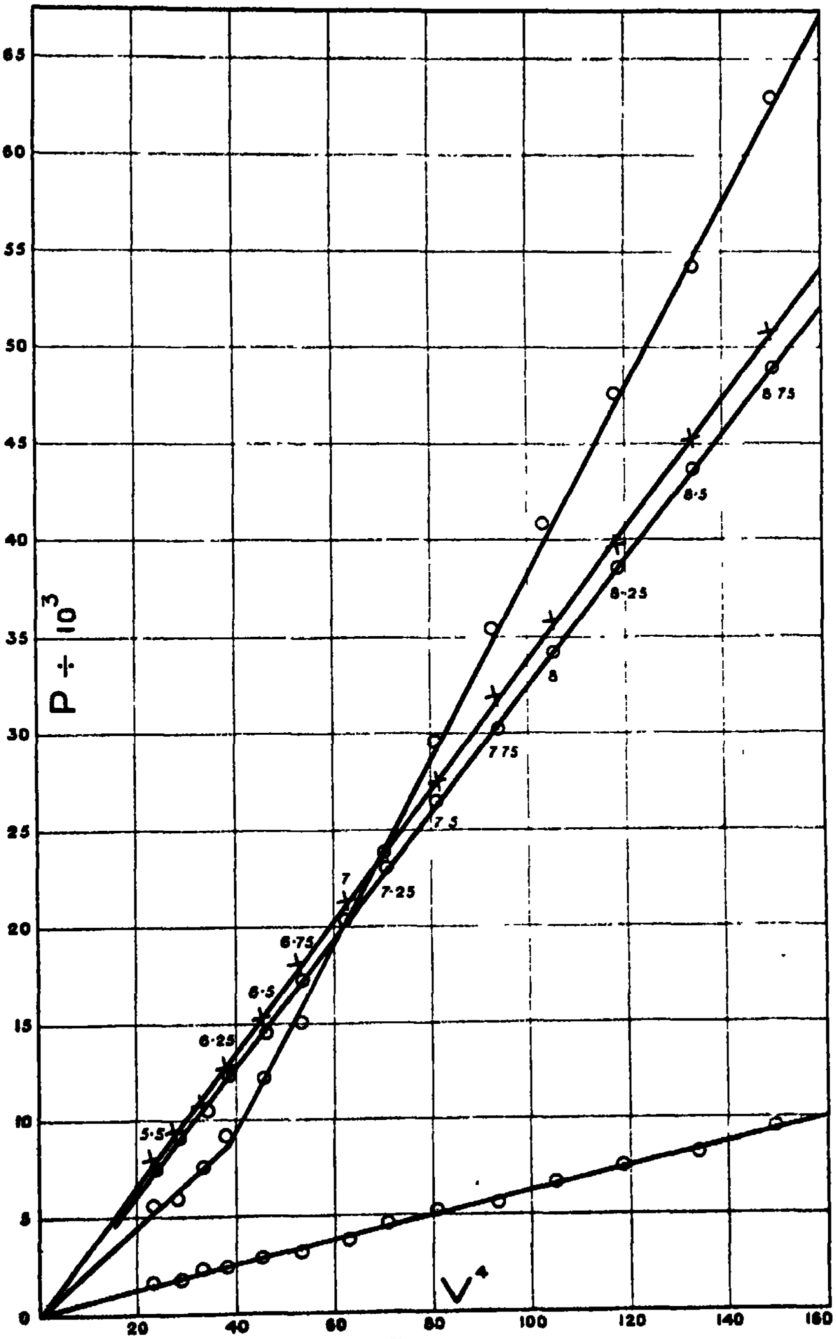
65
60
55
50
45
40
35
30
25
20
15
10
5
0
P ÷ 10³
5·5
6·25
6·5
6·75
7
7·25
7·5
7·75
8
8·25
8·5
8·75
V⁴
20
40
60
80
100
120
140
160

FIG. 7.

$$\frac{\text{Total ionisation current due to X-rays}}{\text{Cathode ray current}} = \frac{1{\cdot}48 \times 10^{-6}}{1{\cdot}99 \times 10^{-6}} = 7{\cdot}422 \times 10^{-1} = 60{\cdot}1\beta^4,$$

where β = fraction of speed of light.

Since the numbers for silver and aluminium are roughly as the atomic weights, and as Kaye* has found the same result to hold for a very large number of elements, we may take for a working rule

$$X = 0{\cdot}58 A\beta^4,$$

where X = total ionisation current due to X-rays per unit of cathode ray current,
A = atomic weight of radiator.

This will only hold in cases where characteristic radiations are not being excited.

Energy of the X-rays.

The next step is to find how much energy the X-rays possess relatively to the energy of the primary cathode rays.

Let X be defined as above and let N mean the number of pairs of ions which would be produced by the primary cathode rays. It is, therefore, also the ratio of the ionisation current due to the cathode rays per unit of cathode ray current.

Then we shall take the fraction X/N as that fraction of the energy of the cathode rays which reappears as X-rays. Is this assumption justifiable? If the X-rays were first transformed into cathode rays, as the case when air is ionised according to Wilson's experiments,† and if no loss of energy accompanied such a transformation, then the relative ionisations would really be a measure of the relative energies.

The author, however, has found‡ that in the ionisation of the vapours and gases SeH_2, AsH_3, $Ni(CO)_4$, direct ionisation is produced in addition to the indirect ionisation through the intermediate production of cathode rays. Possibly this direct effect only happens when the ionised gas has its characteristic radiation strongly excited.

If direct ionisation is also produced in CH_3I then relative ionisations are not necessarily a measure of relative energies. Nevertheless, a consideration of other results leads to the conclusion that the proportionality holds even in such cases. Thus Kleeman§ has found that direct ionisation takes place with γ-rays, and yet the relative number of ions produced by α-, β-, and

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* Kaye, 'Phil. Trans.,' A, vol. 209, pp. 123–151.

† Wilson, 'Roy. Soc. Proc.,' 1912, A, vol. 87.

‡ Beatty, 'Roy. Soc. Proc.,' 1911, A, vol. 85.

§ Kleeman, 'Roy. Soc. Proc.,' 1909, A, vol. 82.

γ-rays keeps remarkably constant as we pass from one gas to another.[*] Barkla[†] has found a similar proportionality for cathode rays and X-rays in the case of H_2S and SO_2. Hence we may assume the same proportionality in the present experiment.

No data exist as to the total number of ions produced in CH_3I by cathode rays. We can, however, calculate the number in air, and for the present we shall assume that the same number would be produced in CH_3I. Glasson[‡] has found that the number of ions of one sign produced per centimetre in air by homogeneous cathode rays varies inversely as the energy E of the rays, or

$$\frac{\partial N}{\partial x} = \frac{a}{E}. \tag{1}$$

When $E = \frac{1}{2}$ mass of electron $\times (4{\cdot}7 \times 10^9)^2$, he found $\partial N/\partial x = 1140$ for air at N.T.P. Thus a works out as $1{\cdot}053 \times 10^{-5}$.

Whiddington[§] has found that the rate of loss of energy of cathode particles in passing through air is given by

$$-\frac{\partial E}{\partial x} = \frac{1{\cdot}75 \times 10^{-15}}{E}. \tag{2}$$

Hence the total number of pairs of ions equals

$$N = \int \frac{\partial N}{\partial x} \partial x = \int \frac{a}{E} \partial x. \tag{3}$$

Therefore, eliminating ∂x between (2) and (3), and putting in the value of a,

$$N = \frac{1{\cdot}053 \times 10^{-5}}{1{\cdot}75 \times 10^{-15}} E = 2{\cdot}28 \times 10^3 \beta^2,$$

if $\beta =$ equals velocity of cathode rays expressed as a fraction of the velocity of light. Hence

$$\frac{\text{X-ray energy}}{\text{Cathode ray energy}} = \frac{X}{N} = \frac{0{\cdot}58\,A\beta^2}{2{\cdot}28 \times 10^3} = 2{\cdot}54 \times 10^{-4} A\beta^2. \tag{4}$$

For example, if a platinum radiator be excited by cathode rays of speed 10^{10} cm./sec., $A = 195, \beta = \frac{1}{3}$, therefore

$$\frac{X}{N} = 5{\cdot}51 \times 10^{-3}.$$

This is the energy of the "independent X-rays"[||]; the characteristic X-rays, which will be excited in this example, will increase the total energy emitted.

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[*] Kleeman, 'Phil. Mag.,' Nov., 1907, p. 631.

[†] Barkla, 'Phil. Mag.,' Feb. 1912, [6], vol. 23, pp. 317–333.

[‡] Glasson, 'Phil. Mag.,' Oct., 1911, vol. 22, pp. 647–656.

[§] Whiddington, 'Roy. Soc. Proc.,' 1912, A, vol. 86.

[||] Beatty, 'Roy. Soc. Proc.,' 1912, A, vol. 87.

Previous Investigations.

Wien,[*] in 1905, investigated the question of the energy carried by X-rays. He used an X-ray tube with a platinum anticathode, and employed a constant potential difference between cathode and anode of 58,700 volts. He measured the energy of the X-rays using both a bolometer and thermopile. The bolometer method gave $X/N = 0{\cdot}00109$; the thermopile gave $0{\cdot}00135$. On calculating the values which would be given by equation (4). we have $A = 195$, $\beta = -0{\cdot}467$. Therefore

$$\frac{X}{N} = 12 \times 10^{-3}. \tag{5}$$

But the cathode rays in Wien's experiment were heterogeneous, so that the energy of the bundle must have corresponded to a smaller potential than 58,700 volts. The author has found that with such high potentials the main stream of cathode rays has a speed corresponding to about two-thirds of the potential as given by the spark gap. When the cathode rays are deflected to give a magnetic spectrum the band of luminosity on the willemite screen is discontinuous, the discontinuities corresponding to the oscillations in the discharge at each break of the primary current in the coil. Five or six such oscillations can usually be recognised by the luminous cathode spectrum, the velocity of the rays decreasing with each successive oscillation. From a study of the heterogeneous cathode rays, when analysed in this way, the author concludes that the number in formula (5) should be divided by six to correspond with the conditions of Wien's experiment. Then

$$\frac{X}{N} = 2 \times 10^{-3}.$$

This is still higher than Wien's results, but allowance for absorption of the soft rays due to the glass may bring the two values close together. Evidently, one cannot correct for the absorption of these soft rays by finding the absorption due to a second piece of glass.

Whiddington[†] found that the energy of the X-rays from a silver anticathode varied nearly as the fourth power of the speed of the cathode rays. He describes the experiment as follows:—

"The first experiment was to see how the actual primary Röntgen-ray energy (E_p) escaping through W depended on the velocity v of the cathode rays striking the anticathode. To do this, the radiator R was replaced by the ionisation chamber I. After correcting the observed values of the ionisation currents for the variations of the absorption coefficients of the Röntgen rays with v, it comes out that Ep (per unit cathode ray current) is nearly proportional to v^4."

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[*] Wien, 'Ann. d. Phys.,' 1905, 18, vol. 5, pp. 991-1007.

[†] Whiddington, 'Roy. Soc. Proc.,' 1911, A, vol. 85, p. 323.

In a subsequent paper, a discussion will be given of the results here described with regard to their bearing upon theories of the method of transference of energy from the cathode ray to the X-ray.

It gives me great pleasure to acknowledge the kindly attitude which Sir J. J. Thomson has continued to assume towards this work.

The Relation between the Crystal Symmetry of the Simpler Organic Compounds and their Molecular Constitution.—Part II.

By WALTER WAHL, Ph.D.

(Communicated by Sir James Dewar, F.R.S. Received June 19,—Read June 26, 1913.)

In this paper the experimental results concerning the crystalline properties of the unsaturated aliphatic hydrocarbons, the simpler oxygen- and sulphur-compounds of carbon, the halogen-compounds, and the simpler aromatic hydrocarbons are given.

Ethylene.—Ethylene, prepared from alcohol and sulphuric acid, was purified by liquefying it and distilling it twice. It crystallises very well, large prisms being formed. Two distinct cleavage systems occur, one parallel to a prism and the other parallel to the basal plane (or an orthodome). The double-refraction is of middle strength; the extinction is in some sections parallel to the prismatic cleavage, in others it is not. The angle of the optical axes is large, and the optical character negative. These optical observations show that ethylene crystallises in the monoclinic crystal system.

Acetylene.—Acetylene which had been prepared from calcium carbide was purified by passing it through a solution of chromic acid in acetic acid, and by subsequently solidifying it by cooling with liquid air. The temperature of the solid mass was then allowed to rise until it began to evaporate, and the first and last portions to evaporate were pumped away, the middle portion only being collected. These operations were repeated twice.

Acetylene cannot be liquefied at ordinary pressure, but is condensed directly in the solid state. If condensed at not too low a temperature, it forms small isotropic crystals, which consist of cubes, the corners of which are cut off by the octahedron. On further cooling, a transition occurs, and the small crystals become strongly double-refracting. This transition takes place very readily and is reversible. If the gas is condensed by rapidly cooling the crystallisation vessel with liquid air, it is condensed directly into the double-refracting modification. This then grows in the shape of small prismatic crystals which exhibit a parallel extinction. This second form of acetylene is therefore tetragonal, hexagonal or rhombic. At certain temperatures both modifications are seen to form simultaneously, and the one subsequently changes rapidly into the other according as the temperature is above or below that of the transition point.

Carbon Monoxide.—Carbon monoxide was prepared by heating a mixture of sodium formate and sulphuric acid and passing the gas through caustic potash solution. It was then purified by condensation and fractionating.

Carbon monoxide crystallises in the regular crystal system. The manner of growth indicates that the prevailing form is that of the rhombic dodecahedron.

Carbon Dioxide.—Carbon dioxide has been investigated by Liversidge,* who found that it crystallises in the regular system. Recently Behnken has described an elaborate apparatus which has been used for the investigation of carbon dioxide and some other gases.† According to the observations of Behnken carbonic acid is regular.

When pure, dry carbon dioxide is condensed in the crystallisation vessel by cooling with liquid air it condenses in the form of small cubes which are quite isotropic. No polymorphic change was observed above −210°.

Carbon Oxychloride.—A bottle containing a 20-per-cent. solution of phosgene in toluene (Kahlbaum) was connected with the condensation vessel of the apparatus used for fractionating the hydrocarbons and the other gases. The whole apparatus was first exhausted and the condensation vessel then cooled in liquid air, and the stopcock separating the phosgene solution from the condensation vessel was then opened. In this way sufficient phosgene was gradually pumped out of the solution and condensed in the crystallisation vessel. It was then allowed to boil off and the higher boiling part collected over mercury. On investigation in the crystallisation vessel, it was, however, found that the entire quantity of the liquefied gas did not crystallise simultaneously, but that small isotropic crystals were deposited on the walls of the crystallisation vessel at a much higher temperature than that at which the principal part crystallised. These crystals apparently belonged to carbon dioxide, and the presence of hydrochloric acid gas was, therefore, also probable, the two being the products of the action of moisture on phosgene. It seems that these admixtures are not sufficiently removed by condensation. The gas was, therefore, admitted to a previously evacuated glass bulb containing a small quantity of metallic sodium, and allowed to remain over this for some time. After this treatment the phosgene was found to crystallise homogeneously.

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* A. Liversidge, 'Chem. News,' vol. 71, p. 152; vol. 77, p. 216.

† H. E. Behnken, 'Phys. Rev.,' 1912, vol. 35, p. 66.

Phosgene is liquid over a considerable range of temperature. On cooling it becomes supercooled, and an unstable modification crystallises, as a rule, out of the supercooled melt. If cooled rapidly, the growth of this modification may be entirely arrested and the remainder of the melt becomes quite viscous. If the preparation is allowed to get warmer after the unstable modification has been formed a transition into the stable form very soon takes place. When this again is partially melted, it crystallises readily on cooling. The stable modification possesses a high double-refraction, but isotropic sections occur also. It belongs, therefore, either to the tetragonal or hexagonal system, but it has not been possible to determine to which of the two, as the cleavage is not very distinct. The optical character of the stable modification is positive. The unstable modification possesses an extremely high double-refraction and shows parallel extinction. It is probably orthorhombic.

Carbon Oxysulphide.—Carbon oxysulphide was prepared by the action of concentrated sulphuric acid on the allyl ether of isosulphocyanic acid. The gas was purified by passing it through wash-bottles containing potassium hydroxide solution and concentrated sulphuric acid. It was then liquefied, and, after a part had been allowed to boil off, a fraction was collected for investigation. Carbon oxysulphide crystallises in extremely fine needles, which grow with great rapidity. The double-refraction of these needles is very high and they always extinguish the polarised light in the position parallel to the principal sections of the nicols. The needles are thus either tetragonal, hexagonal or orthorhombic, but it has not been possible to find any experimental evidence from which conclusions might be drawn as to which of these crystal systems the oxysulphide belongs to. No polymorphic change has been observed above −200°.

Carbon Bisulphide.—Carbon bisulphide crystallises in very strongly double-refracting needles which belong to the monoclinic or triclinic system.*

Methyl Chloride.—Methyl chloride was prepared by heating trimethylamine hydrochloride. The gas was purified by fractionating it. Methyl chloride crystallises from the supercooled melt in form of a fine grainy mass. If part of this is melted and recrystallised, long needles, rapidly growing in several directions, are formed. They are very strongly double-refracting and show parallel extinction. On further cooling a marked cleavage in the longitudinal direction of the needles is developed, but no polymorphic change has been observed at temperatures above −200°. As needles of parallel extinction are seen which exhibit a different strength of double-refraction they cannot belong to the tetragonal or hexagonal system, but are either orthorhombic or monoclinic with a very small angle of extinction on the clinopinakoid.

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* 'Roy. Soc. Proc.,' A, vol. 87, p. 379.

Dichlormethane.—Methylene chloride crystallises well, long prisms being formed which seem to be terminated by a pair of domal faces. The double-refraction is strong and the extinction parallel to the prism axis. This modification of dichlormethane is orthorhombic. At low temperature it changes enantiotropically into a mass of needles of much lower double-refraction.

Trichlormethane.—Chloroform crystallises well. Large crystal fields of strong double-refraction are mostly formed, but occasionally isotropic fields are developed. In one instance one of these grew with a remarkably regular hexagonal outline. Chloroform is thus trigonal or hexagonal. No polymorphic change has been noticed above −200°.

Tetrachlormethane.—Carbon tetrachloride crystallises at −22° in isotropic grains, but when the temperature is lowered a transition into a double-refracting mass takes place at −47°.*

Methyl Bromide.—When cooled, methyl bromide, as a rule, becomes strongly supercooled, but at a very low temperature crystallisation takes place, the resulting product being a fine grainy mass, which shows "aggregate-polarisation." When the preparation is allowed to get warmer gradually, strongly double-refracting prisms of another modification grow slowly in the grainy mass, and at still higher temperature these change into a third modification which also grows in prismatic forms, but is not as strongly double-refracting as the second modification. Very soon after this transition the crystals melt. The second modification has also been obtained directly by crystallisation of the supercooled melt. The transition between Form I and Form II takes place readily in both directions. As stated, Form III on heating grows quite slowly in Form II, and if the preparation is again cooled when only part of III has changed into II, the further growth of II is arrested, but it does not change back into III. This is probably due to a very small velocity of transition, and to the falling-off of this velocity to almost negligible value on lowering the temperature, whereby, at low temperatures, a kind of pseudo-equilibrium between the Forms II and III results.

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* This transition has recently been described by V. M. Goldschmidt, 'Zeitschr. f. Krystallographie,' 1912, vol. 51, p. 26.

The modification I, which is stable at the melting-point, crystallises in the monoclinic crystal-form, and is sometimes twinned according to the orthodome. The extinction angle between the two halves is in maximum only about 12°, which gives an extinction angle of about 6° on the clinopinakoid. The modification II possesses, as already stated, a much stronger double-refraction. It is orthorhombic, or, possibly, monoclinic, with a quite small extinction angle. Of modification III nothing more definite than that it is double-refracting can be said. It has only been observed as a very fine grainy mass. Methyl bromide is thus trimorphic.

Dibrom-methane.—Methylene bromide crystallises readily in long prismatic needles which belong to the orthorhombic crystal system. At a temperature close to −200° a polymorphic transition into another double-refracting modification takes place.

Bromoform.—Bromoform becomes easily supercooled. At temperatures not much below the melting-point the velocity of crystallisation is, however, considerable. Remarkably enough, the crystals are simultaneously developed and grow in two different crystal directions; partly as long narrow laths, and partly as large crystal fields; the former possess a very strong double-refraction and parallel extinction, the latter are isotropic, but show in convergent light the cross of a uniaxial, optically negative crystal. The lath-shaped needles are probably crystals which grow in the direction of a lateral crystal axis, and are developed with the basal plane at right angles to the walls of the crystallisation vessel; the isotropic fields are crystals which grow with the basal plane parallel to the walls. Thus bromoform crystallises in thin hexagonal tablets.

When the temperature is lowered, crystal germs of a second strongly double-refracting modification are formed in great number inside the first modification, but they grow very slowly, and when the temperature is further lowered they entirely cease to grow. Bromoform exhibits thus a case of pseudo-equilibrium between two crystal modifications at low temperature. If the temperature is very suddenly lowered, it is therefore easily possible to cool down the first modification to −180° without any noticeable amount of the second modification being formed at all. When the temperature is then allowed to rise, and the preparation reaches a temperature interval in which crystal-nuclei of the second modification are formed and the velocity of transition attains noticeable values, the crystals I are transformed into a grainy mass of the form II. When a still higher temperature is reached, Form II again changes into Form I, which, on further increase of temperature, melts. In consequence of the passing over of one transition on rapidly cooling, and the pseudo-stability of Form I at low temperature, a change of one form into the other and the reverse change can thus take place without the sense in which the temperature is changing being reversed.

Tetrabrom-methane.—Tetrabrom-methane crystallises in cubic growth-structures, which at +46° change into a monoclinic modification. This latter is also obtained directly by crystallisation from ether, petrol-ether, and other solvents at room temperature. It has been measured by Zirngiebl,[*] who found that it very closely approaches a regular octahedron, although it is monoclinic.

No further transition has been observed at temperatures above −200°.

Methyl Iodide.—Methyl iodide crystallises in long prismatic needles, some showing parallel extinction, and others showing an extinction angle up to about 25°. They belong to the monoclinic system. A twinning parallel to the orthodoma is also sometimes seen. The cleavage, according to a prism, is well developed, and also a second cleavage, parallel to the basal plane or the orthodoma. No polymorphic transition has been observed above −200°.

Methylene Iodide.—The diagram of state of methylene iodide has been investigated by Tammann and Hollmann,[†] who describe the occurrence of four modifications. According to their measurements at high pressures, the modification which at ordinary pressure crystallises out of the molten condition at +5·7°, changes at −6·5° into another modification. This change is stated to be reversible.

On investigating methylene iodide in a similar way to the other substances described in this paper, it was found that the needle-shaped crystals which are formed out of the melt at ordinary pressure are orthorhombic. No polymorphic change has been detected at a temperature slightly below zero, and the crystals remain unchanged down to very low temperature, although they become very cracked. At about −200° an alteration in the crystallised product takes place. It has, however, not been possible to make out whether this depends upon a polymorphic change, which proceeds very slowly, or whether it is due to the separating out from solid solution of some decomposition product of the methylene iodide. The difficulty of arriving at a decision arises from the fact that methylene iodide changes under the action of light sufficiently quickly to exhibit a distinct coloration from dissolved iodine after but a few minutes. It is therefore, practically impossible to investigate the substance in a pure state.

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[*] Compare Groth, 'Chemische Krystallographie,' vol. 1, p. 230.

[†] G. Tammann and R. Hollmann in 'Krystallisieren und Schmeltzen,' Leipzic, 1903 p. 278.

Iodoform.—Iodoform has been investigated crystallographically by Rammelsberg, Kokscharow, and Pope.* It crystallises in the hexagonal system in tablets, which are parallel to the basal plane. Iodoform is partially decomposed when heated to the melting point, and it is therefore difficult to obtain good crystal-growth directly from the melt. It was, however, found that it crystallises from the melt in a very similar way to bromoform. large isotropic fields and narrow double-refracting laths being formed. This corresponds entirely to the growth in tablets which is obtained from solutions. No polymorphic change takes place between the melting-point temperature and room temperature, but it seems that a change takes place in the crystals not far below room temperature. However, since the iodoform is decomposed to a certain extent when melted, it has not yet been possible to make out with certainty whether it is a polymorphic change which takes place, or whether the change is due to the separating out of solid solution of some of the decomposition products.

Methane Tetraiodide.—Methane tetraiodide crystallises, according to Gustavson,† in octahedra, which are isotropic in polarised light, and thus regular.

Mononitromethane.—Nitromethane crystallises very readily, forming large crystal fields, which belong to the monoclinic system. The double-refraction is high. The angle of the optic axes is large, and one of the axes shows a strong dispersion. The optical character is positive. On cooling further, a cleavage parallel to the prism, and a second, but less distinct, cleavage parallel to the basal plane, are formed. No other modification has been observed above −200°.

Tetranitromethane.—Tetranitromethane crystallises in the regular crystal system. At low temperature an enantiotropic transition into another modification takes place. The double-refraction of this modification exceeds in no sections 0·005. It is probably tetragonal or hexagonal.

Chloropicrin.—Chloropicrin crystallises in the shape of long thin needles which possess a strong double-refraction and a parallel extinction. It thus belongs to either the tetragonal, hexagonal, or orthorhombic systems. No other polymorphic modifications have been observed above −200°.

Methyl Alcohol.—Methyl alcohol is monoclinic or triclinic.‡ At low temperature a polymorphic transition takes place.

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* See Groth, 'Chemische Krystallographie,' vol. 3, p. 4.

† G. Gustavson, 'Ann. der Chemie,' vol. 172, p. 173.

‡ See 'Roy. Soc. Proc.,' A, vol. 87, p. 379.

Ethyl Alcohol.—Ethyl alcohol does not crystallise well. It belongs to one of the crystal systems of low symmetry.[*]

Tertiary Butyl Alcohol.—The original sample of trimethylcarbinol prepared by Butlerow was examined crystallographically by Pousirewsky.[†] He states that the alcohol in the anhydrous state crystallises in the shape of six-sided prisms terminated by the basal plane. The angle between the prism faces was roughly measured by Pousirewsky as being 120°, and the angle between the prism faces and the basal plane as being 90°. This would indicate that the crystals belong to the hexagonal system. Pousirewsky, however, found that the crystals are optically bi-axial, the axial plane being parallel to the basal plane. He therefore considered trimethylcarbinol to be orthorhombic but pseudo-hexagonal.

The alcohol was investigated in the same way as the other substances described in this paper, and it was found that, when not quite anhydrous, it crystallises in the shape of needles which grow with great rapidity, when pure crystal fields are formed. Some of them have been found to be isotropic. At a temperature not far below that of the melting point, and several degrees above zero, a transition takes place into another modification which is very similar to the first one. Both modifications possess a low maximum double-refraction. No cleavage has been observed in the first modification, and in the case of the second the cleavage developed at quite low temperature is of an irregular character.

These observations, compared with those of Pousirewsky, show that trimethylcarbinol crystallises from the molten state in hexagonal crystals which already at a temperature above zero change into a very similar but orthorhombic modification without the outer shape of the crystals being changed. Pousirewsky's optical determinations were evidently made at a temperature below that of the transition point, whereby he was led to draw the conclusion that the carbinol was orthorhombic, pseudohexagonal and not really hexagonal.

Dimethyl Ether.—Dimethyl ether was prepared by the interaction of methyl iodide on sodium methylate and the gas was purified by condensation and fractionation. Dimethyl ether crystallises in long narrow prisms which show parallel extinction and possess a very low double-refraction. The ether is rhombic. No other modification has been obtained above −200°.

Methyl-ethyl Ether.—The ether was prepared by the interaction of methyl iodide and sodium ethylate, and purified by condensation and fractionation. Methyl-ethyl ether crystallises in prismatic columns of medium high double-refraction. These belong to the monoclinic or triclinic system. No other polymorphic form has been observed above −200°.

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[*] 'Roy. Soc. Proc.,' A, vol. 87, p. 378.

[†] Butlerow, 'Liebig's Annalen,' vol. 162, p. 229.

Ethyl Ether.—Timmermans[*] has recently found that two modifications of ethyl ether exist, a stable one melting at −116·2° and an unstable one melting at −123·3°. The crystallisation of the stable modification has been described earlier.[†] It crystallises in the rhombic system. If ether is very suddenly cooled, it becomes glassy, and when warmed the unstable modification usually crystallises in beautiful spheruliths showing the "Bertrand cross." This form is much less double-refracting than the stable form. When the temperature rises further, crystal germs of the stable modification are formed; it then grows rapidly inside the unstable modification, just as in the liquid phase. It is remarkable that the growth of the stable form often starts at the centre of the spheruliths of the unstable form.

Acetone.—Acetone crystallises in the monoclinic or triclinic system.[‡] No polymorphic transition has been observed above −200°.

Ortho-ethyl Ether of Carbonic Acid.—When cooled by admitting liquid air to the vacuum-vessel surrounding the crystallisation-vessel the ortho-ethyl-ether of carbonic acid, as a rule, gets supercooled. At a temperature between −180° and −200° the stiff liquid becomes glassy in character and cracks in quite a peculiar manner, giving rise to a product which is absolutely similar in appearance to the perlitic volcanic glasses. If the exhaust on the liquid air is turned off and the preparation is allowed to warm gradually, the perlitic structure disappears as the glass of the ortho-ether warms.

If the stiff liquid is caused to crystallise by rubbing the wall of the vessel with a metal wire a very great number of crystal nuclei are formed, and grow very slowly. The phenomenon has much the same appearance as when ammonium magnesium phosphate is precipitated from a solution by rubbing the walls of the vessel. If the crystallisation vessel in which crystals have previously been formed is slowly cooled, a great number of isolated crystal nuclei appear; these grow on further cooling into small growth-structures with sharp boundary lines. They consist of small flat tetragonal bi-pyramids, the tops of which are cut off by the basal plane. Other sections occur which have grown parallel to the basal plane, and have the appearance of square letter envelopes. These sections are isotropic between crossed nicols. As far as can be estimated under the microscope, the angles of these tetragonal bi-pyramids must be practically those of the regular octahedron. The ortho-ether is thus tetragonal and pseudo-regular.

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[*] J. Timmermans, 'Bull. Soc. Chim. Belgique,' 1911, vol. 25, p. 300.

[†] 'Roy. Soc. Proc.,' A, vol. 87, p. 378.

[‡] See 'Roy. Soc. Proc.,' A, vol. 87, p. 379.

On further cooling the liquid gets quite viscous, and the small octahedra entirely cease to grow, the liquid ultimately becoming a perlitic glass, in which the "porphyric" octahedral crystals lie embedded. This product is very similar to the volcanic glasses containing porphyric felspars and quartz. When this product is allowed to warm gradually the perlitic cracks in the glass at first disappear, and then a devitrification of the glass takes place. Hereby an immense number of very minute grains are formed, which are so small that they are scarcely distinguishable from one another, and appear as a crystallised "ground mass" merely by their action on polarised light. At higher temperatures the size of these grains gradually increases at the expense of their number, and the product finally, before melting, consists of the original, unaltered porphyric growth-structures embedded in a porphyric, "hypidiomorphic" grainy mass. If, again, the melt in which porphyric growth-structures have already been formed is cooled very slowly during the time the crystal-germs are forming and able to grow, it is possible to obtain a product consisting entirely of the crystal growth-structures.

These crystallisation and devitrification phenomena have been described here in detail, because the resulting products are almost identical in appearance with some of the volcanic rocks rich in silica, the genesis of the structure of which has been the subject of much discussion.

Trimethylene.—Trimethylene was prepared from trimethylene bromide in the manner described by Gustavson.* The gas was purified by passing it through bromine and subsequently condensing it and fractionating it.

Trimethylene crystallises very readily, forming large crystal fields. On cooling further two cleavage systems are developed: the one is parallel to the planes of a rhombohedron, the other is parallel to the basal plane. The extinction is parallel to the basal cleavage and bisects the angle of the other cleavage system. The strength of the double-refraction is very different in different crystal directions. The maximum double-refraction, which is about 0·012, is shown by those sections in which the basal cleavage is most distinctly developed. Certain sections are nearly isotropic, but exhibit a kind of undulatory extinction, and on rotating the nicols in some cases faint bluish and yellowish tints are seen, instead of a definite extinction. An investigation of such crystal fields in convergent light shows that trimethylene is practically uniaxial, but optically anomalous.

The dispersion phenomena as seen in convergent light indicate that the interference figure is in reality that of a bi-axial crystal with an extremely small axial angle, the axial angles for red and for blue light standing at right angles to each other, as in the case of some Sanidines and in Brookite, and as is also sometimes seen in optically uniaxial substances which exhibit "optical anomalies." It seems that the extent to which these anomalies in trimethylene are developed depends to a certain degree upon the rapidity with which the cooling takes place; it has, however, not been possible to find a crystal field showing a normal uniaxial interference figure. No other polymorphic modification has been observed above −200°.

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* Gustavson, 'Journ. Prakt. Chemie,' vol. 36, (2), p. 300.

The conclusion to be drawn from these optical properties with regard to the crystal system of trimethylene is, either that it crystallises in the trigonal system but is optically anomalous, or that it crystallises in the orthorhombic system and is pseudo-trigonal. The principal cleavage system must be interpreted as being parallel to the planes of a flat rhombohedron, but the crystals grow in the direction of the horizontal axes, and a second cleavage system parallel to the basal plane is also developed. Judging from the cleavage we thus arrive at the conclusion that the hydrocarbon is trigonal but optically anomalous, and not orthorhombic and pseudo-trigonal; but a quite definite proof in favour of the one or the other alternative cannot be given.

Hexamethylene.—If rapidly cooled hexamethylene becomes a cracked glass. Slowly cooled it can be brought to crystallise, and once crystallised it crystallises readily. It grows in large dendrites, forming cubic gratings. The crystal fields are absolutely isotropic.

At low temperature this cubic modification changes enantiotropically into a double-refracting modification, which grows in a peculiar way in large patches inside the cubic modification, without the general structure due to the crystallisation forms of the original cubic modification being in any way interfered with. The maximum double-refraction of this second form is about 0·012.

Methyl-hexamethylene.—Methyl-cyclohexane becomes invariably glassy on cooling, but if the wall of the crystallisation vessel is rubbed with a metal wire before the cooled liquid has become very viscous, crystallisation can be brought about. Very slowly growing spheruliths are then developed. If the once crystallised mass is melted in part and recrystallised by again cooling the preparation, monoclinic prisms are formed.

The cleavage is parallel to the prism and to the basal plane, the angle between the orthopinakoid and the basal plane being about 75°. The extinction angle on the clinopinakoid is about 15–20°. The crystals are often simple twins according to the orthopinakoid, and each half is polysynthetically twinned according to the basal plane, giving rise to a "herring-bone structure," similar to that of the pyroxenes in the diabasic rocks of the great Whin Sill. No other polymorphic form has been observed above −200°.

Benzene.—Benzene has been investigated crystallographically by v. Groth.[*] It crystallises in the orthorhombic system. Benzene was examined as to the possible occurrence of other polymorphic modifications, but no transition into some other form could be detected above −200°. Also no "monotropic" unstable modifications have been observed.

Toluene.—Toluene crystallises in a very similar way to benzene. It is orthorhombic, and no further modifications have been observed above −200°.

Para-xylene.—Para-xylene has been investigated crystallographically by Jannasch.[†] It is monoclinic. No other polymorphic modification has been observed above −200°.

Mesitylene.—From the moderately supercooled melt glass-spherulites and small strongly double-refracting needles are formed. After the preparation has been caused partially to melt the recrystallisation takes place with great velocity, prismatic crystals of high double-refraction and parallel extinction being formed. On further cooling a very distinct prismatic cleavage and a perhaps still better developed cleavage parallel to the basal plane are formed, but no polymorphic transition has been observed above −200°.

If the liquid, however, is strongly supercooled before crystallisation sets in, a second unstable modification of very strong double-refraction is formed. This modification is also orthorhombic, and can be melted and recrystallised from the melt in the absence of the stable modification. The unstable modification, however, passes slowly into the stable one, once this is formed, and grows just as crystals grow in a viscous liquid.

Both modifications of mesitylene are orthorhombic.

Hexamethyl-benzene.—Hexamethyl-benzene crystallises similarly to benzene in orthorhombic prisms of strong double-refraction. No polymorphic transition has been observed above −200°, nor any unstable modifications.

Hexachloro-benzene.—Hexachloro-benzene also crystallises in orthorhombic prisms.

Diphenyl-methane.—Diphenyl-methane crystallises in orthorhombic needles.

Tetraphenyl-methane.—Tetraphenyl-methane crystallises from benzene-solution in the shape of needles.[‡] Through the kindness of Prof. Gomberg the author has had the opportunity of examining, in polarised light, the tetraphenyl-methane prepared by him. The crystals which are formed on solidification from the molten state are identical in character with those crystallising out of solutions. According to their optical properties they are orthorhombic. No other polymorphic modification has been observed above −200°.

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[*] v. Groth, 'Jahresberichte d. Chemie,' 1870, p. 2.

[†] P. Jannasch, 'Ann. d. Chemie,' vol. 171, p. 79.

[‡] A. Gomberg, 'Ber. Deutsch. Chem. Ges.,' 1897, vol. 30, p. 2043; and 1903, vol. 36, p. 1090.

Further Investigation of Trimethyl-methane.—As it was not possible previously to obtain crystals other than such as had grown in one certain crystal direction,[*] the investigation of trimethyl-methane has been renewed several times, and fresh samples of the gas prepared and investigated in crystallisation vessels of different size and width. After many vain attempts growths in several directions have been obtained by cooling very rapidly, and it has been established that the way in which the hydrocarbon crystallises is very similar to that of trimethylene, which has been described above. Certain sections are practically dark between crossed nicols, but show in convergent light a cross which is opening slightly. The dispersion phenomena are in this case not as pronounced as in the case of trimethylene. The optical character of trimethyl-methane is negative. Besides the cleavage which in the earlier stage of the investigation was regarded as being parallel to a prism, but is now considered as being parallel to the basal plane, a rhombohedral cleavage also occurs. Trimethyl-methane is thus either trigonal and optically anomalous, or rhombic, but pseudo-trigonal; but more probably the former.

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[*] See 'Roy. Soc. Proc.,' A, vol. 88, p. 359.

Note on Electric Discharge Phenomena in Rotating Silica Bulbs.

By the Hon. R. J. Strutt, M.A., Sc.D., F.R.S., Professor of Physics,
Imperial College of Science, South Kensington.

(Received July 22, 1913.)

The late Rev. F. J. Jervis Smith described some curious experiments on this subject before the Royal Society,* without, however, offering any interpretation of his results. I have recently repeated most of his experiments, and have made others which have thrown light on the matter. As the result, it does not seem that anything fundamentally new as to the mechanism of discharge is to be learnt from this line of research. Still, the work is worthy of brief record, if only to save others the trouble of traversing the same ground.

Jervis Smith's fundamental experiment† is as follows: The exhausted bulb is placed near a body charged to 1,000 volts or more. When the bulb is rotated, a luminous glow is maintained within it. It is not difficult to foresee this result. The rarefied gas may be regarded as a conductor. Suppose the body negatively electrified. Then, since the potential on the inside of the bulb is lower near the outside electrified body than elsewhere, positive electricity will flow to this neighbourhood and negative electricity to other parts of the bulb, until the electric field inside the bulb is nearly neutralised. When the bulb is rotated, these induced charges will be carried round with it, and will have to flow through the gas to recover their equilibrium position. In doing this they set up the ordinary luminosity of discharge. To predict the precise direction of the stream lines would be very difficult, and it does not appear that much would be gained by success. As regards the detailed effects of magnetic fields in various directions in deflecting the luminosity the same may be said. I find that, just as in ordinary discharge tubes, the luminosity at low vacua is mainly that characterising the residual gas, while at high vacua the fluorescence of the silica under cathode rays predominates.

In Jervis Smith's third paper, he describes luminosity produced by rubbing the outside of the rotating silica vessel. I have used the dry hands as rubbers, almost enclosing the bulb in the two palms. The luminosity is then very bright and, under certain conditions, it survives after the rubbing is over.

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* 'Roy. Soc. Proc.,' 1908, A, vol. 80, p. 212; 1908, A, vol. 81, pp. 214, 430.

† I find, however, that this experiment, and also the experiment of producing luminosity in an exhausted globe by rotating it under a rubber, were described as long ago as 1709 by F. Hawksbee, F.R.S., 'Physico-mechanical Experiments on Various Subjects,' pp. 36, 62.

The cause of luminosity is not materially different from what it was in the previous case. Before considering it some experiments will be described:—

(1) On a favourable dry day the bulb was rubbed. Removing the hands and having the bulb rotating at a distance from other objects, the luminosity was extinguished. But on bringing the hand or any other earthed conductor near (not touching), the luminosity was restored.

(2) The rotating bulb was rubbed. A brass cylinder a little larger was then placed co-axially over it. No luminosity could be seen. Displacing the cylinder to one side, still without touching, luminosity was restored.

(3) The bulb was rubbed. An earthed conductor was then adjusted near it, inducing luminosity as in (1). A bunsen burner was passed underneath for a moment to discharge electrification, the top of the flame was not allowed to approach nearer than 3 or 4 inches below the bulb, and did not warm it perceptibly. Luminosity was permanently extinguished.

(4) The electrification produced on the outside of the bulb by rubbing with the hand is positive. This was proved by lowering it into a Faraday cylinder connected with an electroscope charged with electricity of known sign.

Let us for simplicity suppose that the rubber has been removed, leaving the outer surface of the bulb uniformly electrified. Then, if the surroundings in which the bulb rotates are symmetrical about the axis of rotation, no electric field will be created within the bulb. But if an earthed conductor is situated on one side of it, the potential of an element of area of the inner surface will be lowered when that element passes near the conductor. Thus, positive electricity will flow to the point in question, and negative electricity away from it to other portions of the bulb. As before, the charges which have thus attached themselves to the inner walls are continually carried round, and have to flow back through the gas to their equilibrium position.

Another of Jervis Smith's experiments may be referred to which does not fall very well under the title of this note. If a brush discharge from an induction coil is merely allowed to play over a highly exhausted silica bulb like that used in the rotation experiments, the bulb remains brightly luminous afterwards, sometimes for several minutes. In repeating the experiment, I find that this luminosity shows curious flickerings, which are greatly accentuated if earthed conductors are brought near the bulb, and then removed. If the bulb is held for a moment high above a bunsen flame, or if it is breathed upon, the luminosity ceases. As before, the luminosity is connected with electrification of the outside surface. This electrification is initially uneven, and, as the charge creeps over the surface, currents flow through the rarefied gas inside. The approach of earthed conductors also upsets the uniformity of potential inside, and produces the same result. It is certainly curious that these effects should be so persistent. It need scarcely be said that they have merely a superficial resemblance to the afterglow phenomena due to chemical changes in the gas, which I have examined in previous papers.

Finally, it remains to consider one more of Jervis Smith's experiments. which, indeed, first attracted me to the subject. His description runs thus:—

"A silica glow bulb was rotated as before. The camel-hair rubber, after being in contact with the bulb, was removed, and no glow was visible; but, on establishing the magnetic field (about 800 C.G.S. units intensity), the bulb instantly glowed brightly, the glow lasting in some cases eight minutes before it died out. When pointed pole pieces were used on either side of the rotating bulb, a bright equatorial* band about 5 mm. wide of greenish glow was generated."

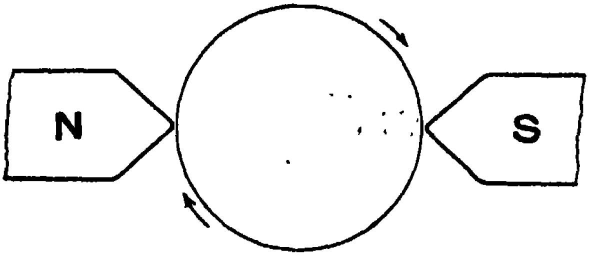

Fig. 1.

I have repeated this experiment without difficulty (fig. 1). As before, it depends on electrification of the bulb surface. Diselectrification by a flame destroys the effect.

Each pole of the magnet, acting merely as an earthed conductor, lowers the potential of the inner surface of the bulb near it, so that these two portions of the surface tend to act as cathodes. The electric force may not be enough to cause discharge; but when the magnet is excited it produces a magnetic force parallel to the electric force, and this, as is known,† lowers the discharge potential so that discharge can occur. At the same time a beam of "magnetic rays"‡ proceeds from each cathode towards the other, along the magnetic lines. These constitute the luminous band described. To my eyes it is blue, not green.

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* The magnetic force is perpendicular to the axis of rotation. The band is equatorial with reference to the latter and stretches between the pole pieces.

† See Birkeland, 'Compt. Rend.,' Feb., 1898, vol. 121, p. 586.

‡ It is not necessary here to enter on the difficult question of the nature of these rays. For our purpose they are simply cathode rays modified by longitudinal magnetic force.

On the explanation given, the ends of the luminous band are each cathodes other parts of the bulb surface acting as anode. It may be objected that the appearance of the band suggests a discharge from one end of it to the other. The experiment indicated in fig. 2 with discharge in a stationary vessel answers this objection; C and C are each flat metal cathodes, and are connected together by a wire. A is anode. N and S are hollow pole pieces of an electromagnet.

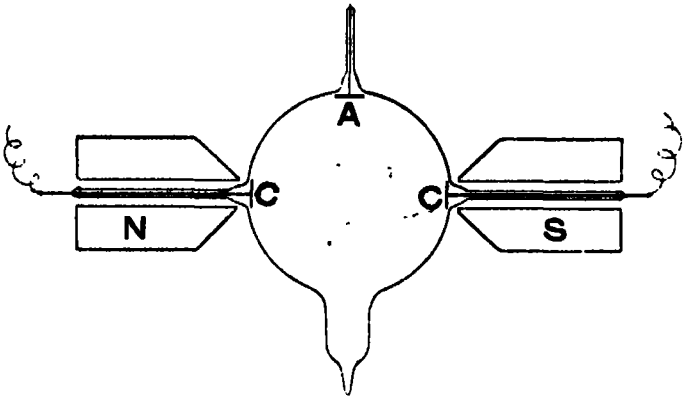

FIG. 2.

A Wimhurst machine is used. At suitable rarefaction, no discharge occurs unless the magnet is excited. When it is excited, a band of negative glow stretches across as shown, exactly like that observed in the rotating vessel. A little positive light can be seen near the anode A, but it is inconspicuous.

Going back to the rotating vessel, these magnetic rays ought not to be seen if the bulb becomes negatively electrified by friction, for then the parts of the inner surface near the magnet poles would act as anodes, not as cathodes.

An exhausted glass bulb was heated and coated with sealing wax over a zone equatorial to the axis of rotation. While being rubbed with silk it was luminous, but the insulation was apparently not good enough to get luminosity when the rubbing had been discontinued. To examine the magnetic effect, rubbers were held near each of the pole pieces of the magnet. Under these conditions the magnetic rays had been brilliant, using the quartz bulb. With the glass one coated with sealing wax, no magnetic rays were seen; on the contrary, when the magnetic force was strong, the luminosity (apparently a cathode ray phosphorescence of the glass) was concentrated in rings lying in the zone of friction, which were nearly great circles, and of nearly uniform brightness all round.

In this case the cathodic portions of the zone which is being rubbed are those distant from the magnet poles. The cathode rays experience not a longitudinal but a transverse magnetic force, and are curled up into small circles, so as to strike the walls again near their point of origin, and produce phosphorescence there. It is true that at any one moment only a portion of the zone is under excitation, but each portion is excited successively, and the phosphorescence lasts long enough to produce sensible uniformity of illumination.

The Origin of Thermal Ionisation from Carbon.

By J. N. Pring, D.Sc.

(Communicated by Prof. E. Rutherford, F.R.S. Received July 26, 1913.)

It has been shown by the present writer in conjunction with A. Parker* that the ionisation which is produced by carbon at high temperatures, and in presence of gases at low pressures, is reduced to a much smaller order of magnitude by eliminating impurities from the carbon, and by exhausting to a high degree the containing vessel.

The results threw considerable doubt on the whole basis of the theory of electronic emission from incandescent solids.

According to this theory,† the ionisation produced by elements at high temperatures is due to the escape of free electrons which pass into the surrounding space on account of the kinetic energy acquired at the high temperature.

It was shown, however, in the above work that in the case of carbon this ionisation is probably related to some chemical action or some intermediate effect exerted by the gas in contact with the solid.

Fredenhagen,‡ who made measurements with sodium and potassium in a high vacuum, came to similar conclusions with regard to the validity of the above theory of electronic emission.

Harker and Kaye,§ in investigating the large ionisation currents from carbon in gases at atmospheric pressure, conclude that an important part is played by the presence of impurities. The ionisation from metals was also considered to be largely affected by the presence of occluded gases.

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* 'Phil. Mag.,' 1912, vol. 23, pp. 199.

† Richardson, 'Phil. Trans.,' 1903, A, vol. 201, p. 497; 'Phil. Mag.,' 1912, vol. 24, pp. 737–744; *ibid.*, 1913, vol. 26, p. 345.

‡ 'Verh. Deutsch. Phys. Gesell.,' 1912, vol. 14, pp. 384–394.

§ 'Roy. Soc. Proc.,' 1912, A, vol. 86, pp. 379–396; *ibid.*, 1913, A, vol. 88, pp. 522–538.

Richardson,[*] in discussing the results of Pring and Parker, admits that the ionisation originally measured by him in the case of carbon was largely influenced by the presence of impurities leading to chemical reaction. The result of this was to lead to an abnormally high value being given to the constant A in the expression $A\theta^{\frac{1}{2}}e^{-Q/2\theta}$, which was deduced to represent, on the basis of the thermionic theory, the relation between ionisation and temperature. By revising the constants from which the values in this formula are derived, the formula was made to follow much more closely the experimental results of Pring and Parker, though it still gave values considerably higher than the latter, and did not agree with the observed influence of temperature. It was, however, maintained that the fundamental theory put forward by Richardson, accounting for the relation between ionisation and temperature, was not disturbed.

Scope of Experiments.

The aim of the present work was to see if any direct electronic emission can be attributed to incandescent carbon, when the large ionisation effects, which were found in the earlier work to be due to chemical action, were more completely removed.

For this purpose the purification of the carbon and the exhaustion of the surrounding vessel were carried out more extensively than before, and the effect on the ionisation at definite temperatures was carefully measured.

A series of experiments was also made in which small quantities of the highly purified gases—helium, argon, nitrogen, hydrogen, carbon monoxide, and carbon dioxide—were admitted to the vessel at known pressures, to see if any relation could be traced between the ionisation and the relative chemical action of these gases on carbon.

Apparatus.—The apparatus used was of the same type as that in the earlier work. The carbon was mounted in water-cooled holders, as shown in fig. 1. The copper tubes (A, A) served for the introduction of the current used to heat the carbon. Air-tight connections with the side tubes of the flask were made at *b*, *b*, by means of soft wax. The carbon used was in the form of a rod, 8 cm. long and 0·5 cm. diameter, and contained a hollow space in the centre, 1·5 mm. diameter.

The sample used in the measurements was kindly presented to the writer by Dr. J. A. Harker, and was part of some material which had been carefully purified before compressing in the rod form. Further purification was carried out in this work, after mounting in the apparatus, by heating for long intervals at very low pressures. The carbon rod had a resistance of about 0·25 ohm, and by passing a current of 80 ampères at 20 volts a temperature of 1850° was attained when the pressure was below 0·005 mm.

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[*] 'Phil. Mag.,' 1912, vol. 24, p. 737.

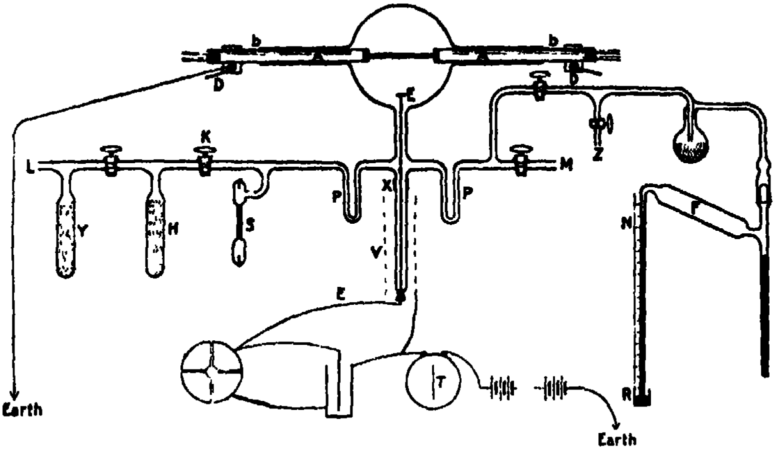

Fig. 1.

For the ionisation measurements, one of the terminals (D) was connected to earth, and a source of positive potential applied to the wire E, to which was connected a small disc. This disc was placed at a distance of about 8 cm. from the heated carbon. Since a potential of 220 volts was applied in the case of all comparative measurements, it could be assumed that the greater part of the ions produced in the vessel would be collected.

A number of experiments were made with a vessel which was coated with silver on the inside, and the metal lining was then used as the anode. After heating for some time, the conductivity became very uncertain, so that this method was abandoned in favour of the disc anode.

A complete collection of the ions was not essential in these measurements, as the ionisation currents varied over such a large range under changing conditions. It became only necessary to consider the order of magnitude in interpreting the results.

The exhaustion of the vessel was effected by means of a Gaede mercury pump connected to the apparatus at M. The higher pressure side of this pump was exhausted by a Sprengel pump. In addition to this, the charcoal tube H, which was cooled by liquid air, was also applied for the final exhaustion of the main apparatus. After removal of the liquid air, the charcoal was always disconnected from the main apparatus by means of the tap K, and before each experiment was exhausted continuously for at least 12 hours, by means of the Sprengel pump connected to L, while the temperature was kept at about 400° by a surrounding electric furnace.

A Töpler pump of large capacity at F was used for preliminary exhaustions and for the removal of gases which it was desired to collect. This pump also served as a pressure gauge, by using the scale placed behind the capillary at N. The column of gas in the capillary was arrested and measured when it stood at a height of 70 cm. above the reservoir R. The calibration showed that a column 1 cm. high corresponded to a pressure in the apparatus of 0·003 mm. This enabled a measurement to be made within 0·0001 mm. in the absence of condensable gases.

The U-tubes (P, P), which were surrounded by liquid air during the experiments, were used to condense mercury vapour in order to protect the charcoal from this metal, and also in order to condense any impurities arising from the grease of the taps.

A spectrum tube connected at S was used for the purpose of spectroscopic examination of the gases present, and to obtain an idea of the pressure when below the limits of measurement by the mercury gauge.

The degree of exhaustion obtained with this apparatus when the carbon was cold could not be measured by any of the methods available. No trace of discharge was visible in the spectrum tube on connecting with an induction coil, which, in air, gave a 5-inch spark. However, even after prolonged use of the apparatus, detectable quantities of gas always appeared when the temperature of the carbon was taken above about 1300°. The lowest pressure obtained, when the carbon was at 1900°, was estimated by the mercury gauge at 0·0002 mm., but in most cases it could not be reduced below 0·001 mm. at this temperature.

Temperature Readings.—These were made with a Wanner optical pyrometer sighted directly on to the heated carbon. The pyrometer was first carefully calibrated and standardised by comparing with a thermo-junction pyrometer, and at the melting points of pure platinum and iridium.* It was ascertained in some earlier measurements that the absorption of the light by the clean glass of the vessel did not cause an error exceeding 10° in the measurement.

On account of the possibility of error in hurried individual measurements, a large number of readings were first taken at different temperatures, and at a pressure of 0·001 cm., and the values were plotted (watts against temperature) in the form of a curve.

Since readings of the current and voltage were made in every case, this curve was referred to in all subsequent readings, and in many cases a direct temperature reading during the actual experiment was avoided altogether. The curve was determined after the carbon showed no further change in resistance with continued heating.

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* See Pring, 'Lab. Exercises in Phys. Chem.,' Manch. Univ. Press, p. 154.

By comparing the values obtained by the different methods used for calibrating the pyrometer, and by considering the degree within which carbon radiates as a black body,[*] it was found that an accuracy to within 25° could be relied on at 1300° in the temperature measurements and within about 60° at 2000°.

Measurement of Ionisation.

The source of positive potential, usually 210–220 volts, which connected with the anode wire E, was first passed through a water resistance of about 1 megohm. For the measurement of the larger ionisation currents a milliammeter or galvanometer was inserted in the circuit at T. For the smaller currents, a Dolezalek electrometer was used in parallel with standard capacities ranging from 0·001 to 0·3 microfarad.

The wire leading from the electrometer was encased in an insulated metal tube, which, together with a metal cylinder placed around the lower part of the glass vessel at V, a narrow guard-ring of tin foil at X, and metal plates placed under the galvanometer and electrometer, was connected to the source of positive potential, in order to prevent any leak from the insulated anode to earth.

When using the full potential a voltmeter was connected to the circuit immediately before and after each series of measurements. In order to ascertain the actual potential applied in the cases where larger ionisation currents were obtained, and where a fall of potential through the water resistance would result, the voltmeter was connected permanently between the earth wire and the further side of the galvanometer. A number of additional readings were taken at a lower potential by using a source of 100 volts, and cutting down by means of the resistance.

The Dolezalek electrometer gave a scale deflection of 1 cm. per minute when used with 0·001 mf. capacity, with a current of 3×10^{-12} ampère. No detectable leak occurred through the apparatus when cold, and by applying an additional potential of 2 volts by means of a cell, on to the insulated electrometer wire, no appreciable leak to any of the surrounding metal guards could be observed. Since the surface of the carbon was 13 sq. cm. all the ionisation values below have been divided by this figure, in order to give the current per square centimetre of surface.

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[*] *Ibid.*, p. 157.

The experiments recorded in this paper were carried out after the carbon had been subjected to prolonged heating in a high vacuum, and was not capable of further purification by this treatment.

Preparation of Gases.

Nitrogen.—The gas was prepared by heating ammonium nitrite, storing in a gas-holder, and then after drying was passed through molten phosphorus and through a spiral cooled by liquid air, and then into a vessel containing mercury.

This gas was admitted in small quantities to the main apparatus through the tap Z (fig. 1) by first filling the small space between this and a second tap connecting with the gas-holder.

The results of the ionisation measurements are given in Table I, and are plotted in the form of curves for the different temperatures (fig. 2). The ordinates represent the logarithm of the ionisation and the abscissæ the pressure.

Hydrogen.—This was prepared by electrolysing baryta, and, after passing over heated platinised asbestos, calcium chloride, and phosphorus pentoxide, the gas was absorbed by palladium foil contained in a glass tube and warmed by an electric furnace. One end of the tube connected directly to the main apparatus at Z (fig. 1), and when the palladium was cold, the end leading to the generator was closed by means of a tap and the tube exhausted by means of the Töpler pump, and finally by the Gaede pump on the main apparatus. By then warming the palladium and regulating the connecting taps, definite quantities of hydrogen were admitted to the reaction vessel. The results of the ionisation measurements obtained are shown in Table II, and in fig. 3.

Carbon Monoxide.—This was prepared by the action of formic acid on heated sulphuric acid, and, after passing through a concentrated potassium hydrate solution, was admitted to a thoroughly exhausted vessel of 50 c.c. capacity, which was fitted with a tap and contained some phosphorus pentoxide. The gas was allowed to remain in this tube for 15 hours, and then admitted to the reaction vessel through the tap Z, as in the case of the nitrogen. In all these experiments where gases were admitted to the reaction vessel, the U-tube P would remove any condensable impurity.

The results of these measurements are shown in Table III and in fig. 4, as before.

Carbon Dioxide.—This was obtained from a cylinder of commercial gas, and, after storing in a bulb, was admitted directly into the apparatus. The measurements made with this are shown in Table IIIA, and also on fig. 4.

Helium.—This was extracted from samarskite, and, after removal of water vapour and most of the hydrogen by admitting to charcoal cooled by liquid air, the gas was passed over heated copper oxide, and then stored in a tube. Before admitting to the apparatus through the tube L the gas was exposed for a few minutes each in succession to the two charcoal tubes Y and H, which were cooled by liquid air.

Readings with this gas are given in Table IV and fig. 5.

Argon.—This was prepared by passing atmospheric nitrogen over finely powdered calcium carbide mixed with a small quantity of calcium chloride and heated in an iron pipe fitted with water-cooled jackets at the ends. The unabsorbed gas was then passed several times over calcium in a smaller tube, over heated copper oxide, and then dried by phosphorus pentoxide.

The gas was then finally purified by exposing to an electrical discharge in a tube in which the cathode consisted of a liquid alloy of sodium and potassium (70 per cent. potassium). The tube arranged for this had a capacity of about 100 c.c. Two right angle bends were provided, and platinum wires sealed in the walls, one at the end making connection with the liquid alloy, and the other joining on to an aluminium electrode at a distance of 8 cm. from the lower electrode.

A trial was first made with this tube by admitting nitrogen to a pressure of 1 cm. and connecting the tube to a small pressure gauge. After passing the discharge for 8 minutes this gas was so completely absorbed as to stop the discharge. The impure argon was then admitted to a pressure of about 1 cm., and the discharge passed for a few hours. A quantity of this gas was then admitted to a carefully exhausted spectrum tube, and examined spectroscopically. No nitrogen could be detected, though hydrogen lines were present, presumably arising from the electrodes.

The argon was admitted to the apparatus by connecting the tube to Z. The readings obtained with this gas are shown in Table V and in fig. 6.

In the curves for argon and helium, the ordinates, on account of their lower value, are plotted on twice the scale used for the other gases.

The values of all the readings taken at the equilibrium stages are entered in the tables, and these have been plotted on the diagrams in every case when the value came within the range of the axes, and when the potential employed had been 210–220.

Procedure of Experiment.

The apparatus was first evacuated as described above, and after any admission of gas containing moisture, was first allowed to stand several days in presence of phosphorus pentoxide, after carefully exhausting. During this interval no rise of pressure could, as a rule, be observed.

If the carbon was maintained at 1300° and the taps leading to the pumps were closed, the rise of pressure in 5 minutes was usually too small to measure, but above this temperature it became important, amounting at 1800° to about 0·003 mm. in five minutes. It would be expected that some of the gas arising in these cases would result from the decomposition of traces of hydrocarbons given from the wax seals used to hold the water-cooled tubes.

In the experiments which were conducted at the lowest pressures, the exhaustion of the vessel was continued throughout the measurement. When using purified gases, a small quantity of the gas was admitted after first closing the taps leading to the pumps, adjusting the temperature of the carbon by means of rheostats, and completing all the electrical connections on the high potential circuit. Readings of the ionisation current were then made by means of the electrometer or galvanometer, immediately after the admission of the gas, and then at definite intervals. These were followed by readings of the pressure and temperature as described above.

Comparative experiments were conducted from time to time by exhausting the vessel, closing all taps, and noticing the increase of ionisation with time due to the increase of pressure which gradually took place at the high temperatures.

Tabulation of Results.

Table I.—Nitrogen (pure).

Temp.	Pressure.	Ionisation.	Temp.	Pressure.	Ionisation.
Potential Difference 210–220 volts.					
°	mm.	amp. per sq. cm.	°	mm.	amp. per sq. cm.
1130	0·001	$8·5 \times 10^{-13}$	1615	0·002	$5·8 \times 10^{-10}$
1150	0·3	$3·8 \times 10^{-8}$	1630	0·009	$3·2 \times 10^{-7}$
1200	<0·0001	$2·3 \times 10^{-12}$	1650	0·03	$3·8 \times 10^{-6}$
1270	0·003	$2·4 \times 10^{-11}$	1750	0·0015	$7·7 \times 10^{-9}$
1270	0·3	$6·1 \times 10^{-7}$	1830	0·004	$4·5 \times 10^{-6}$
1280	<0·0001	$3·1 \times 10^{-13}$	1840	0·03	$2·2 \times 10^{-4}$
1280	0·001	$8·9 \times 10^{-12}$	1900	0·0002	$1·3 \times 10^{-9}$
1325	0·0006	$2·8 \times 10^{-11}$	1900	0·0004	$2·4 \times 10^{-9}$
1350	0·0001	$1·9 \times 10^{-11}$	1900	0·0007	$4·8 \times 10^{-9}$
1370	0·0016	$1·4 \times 10^{-10}$	1900	0·001	$5·4 \times 10^{-9}$
1410	0·005	$1·6 \times 10^{-9}$	1900	0·0016	$9·4 \times 10^{-9}$
1440	0·001	$2·4 \times 10^{-10}$	2000	0·002	$2·4 \times 10^{-8}$
1450	0·0001	$1·7 \times 10^{-10}$	2020	0·0015	$1·2 \times 10^{-8}$
1610	0·0006	$3·0 \times 10^{-10}$	2025	0·0006	$8·5 \times 10^{-9}$
1610	0·003	$1·7 \times 10^{-9}$			
Potential Difference 100 volts.					
1285	0·0001	$1·57 \times 10^{-10}$	1630	0·0006	$4·0 \times 10^{-9}$
1365	0·0001	$3·3 \times 10^{-10}$	1890	0·001	$1·5 \times 10^{-8}$
1475	0·0003	$9·7 \times 10^{-10}$	1900	0·0005	$2·7 \times 10^{-9}$

These results, which are plotted in the form of curves in fig. 2, show the very large part played by the pressure of the surrounding gas. At low pressures, however, the *ionisation* approaches a *limiting* value *for each* temperature. As discussed below, this is probably due to the occlusion of residual gas.

Table II.—Hydrogen.

Potential 210–220 volts.			Temperature 1350°.		
Temp.	Pressure.	Ionisation.	Potential.	Pressure.	Ionisation.
°	mm.	amp. per sq. cm.	volts.	mm.	amp. per sq. cm.
1200	<0·0001	$2{\cdot}3 \times 10^{-12}$	100	1·0	$5{\cdot}5 \times 10^{-2}$
1200	0·0002	$3{\cdot}1 \times 10^{-12}$	85	1·0	$1{\cdot}8 \times 10^{-2}$
1200	0·001	$6{\cdot}8 \times 10^{-12}$	95	1·0	$5{\cdot}0 \times 10^{-2}$
1200	0·002	$9{\cdot}3 \times 10^{-12}$	93	1 0	$1{\cdot}3 \times 10^{-2}$
1200	0·003	$1{\cdot}2 \times 10^{-11}$	115	0·03	$4{\cdot}5 \times 10^{-2}$
1200	0·0075	$2{\cdot}1 \times 10^{-10}$	100	0·03	$4{\cdot}5 \times 10^{-2}$
1200	0·16	$1{\cdot}5 \times 10^{-9}$	75	0·03	$3{\cdot}5 \times 10^{-2}$
1200	0·4	$1{\cdot}0 \times 10^{-8}$	65	0·03	$2{\cdot}5 \times 10^{-2}$
1340	0·0002	$1{\cdot}6 \times 10^{-11}$	40	0·03	$1{\cdot}0 \times 10^{-2}$
1340	0·002	$4{\cdot}4 \times 10^{-11}$			
1340	0·003	$7{\cdot}7 \times 10^{-11}$			
1340	0·006	$1{\cdot}5 \times 10^{-6}$			

These values are plotted in the form of curves in fig. 3, where the abscissæ denote the pressures, and the ordinates the logarithm of the ionisation currents.

Table III.—Carbon Monoxide. Potential 210–220 volts.

Temp.	Pressure.	Ionisation.	Temp.	Pressure.	Ionisation.
°	mm.	amp. per sq. cm.	°	mm.	amp per sq. cm.
1180	<0·0001	$1{\cdot}5 \times 10^{-12}$	1280	0·003	$1{\cdot}1 \times 10^{-9}$
1180	0·001	$3{\cdot}85 \times 10^{-12}$	1315	0·002	$4{\cdot}8 \times 10^{-11}$
1180	0·002	$1{\cdot}0 \times 10^{-11}$	1340	0·0012	$1{\cdot}2 \times 10^{-11}$
1180	0·005	$2{\cdot}7 \times 10^{-10}$	1410	0·002	$2{\cdot}5 \times 10^{-10}$
1180	0·006	$3{\cdot}0 \times 10^{-10}$	1410	0·007	$1{\cdot}8 \times 10^{-8}$
1180	0·03	$2{\cdot}3 \times 10^{-8}$	1550	0·0015	$1{\cdot}3 \times 10^{-9}$
1180	0·7	$1{\cdot}7 \times 10^{-8}$	1550	0·002	$3{\cdot}8 \times 10^{-9}$
1280	<0·0001	$2{\cdot}15 \times 10^{-12}$	1550	0·0045	$1{\cdot}0 \times 10^{-6}$
1280	0·0015	$1{\cdot}0 \times 10^{-11}$	1720	0·002	$>4{\cdot}0 \times 10^{-6}$

Table IIIa.—Carbon Dioxide. Potential 210–220 volts.

Temp.	Pressure.	Ionisation.	Temp.	Pressure.	Ionisation.
°	mm.	amp. per sq. cm.	°	mm.	amp. per sq. cm.
1160	0·003	$2{\cdot}3 \times 10^{-8}$	1180	0·003	$3{\cdot}8 \times 10^{-8}$
1180	0·004	$5{\cdot}1 \times 10^{-10}$	1370	0·003	$3{\cdot}1 \times 10^{-7}$

The results with carbon monoxide and dioxide are also shown in fig. 4.

Table IV.—Helium. Potential 210–220 volts.

Temp.	Pressure.	Ionisation.	Temp.	Pressure.	Ionisation.
°	mm.	amp. per sq. cm.	°	mm.	amp. per sq. cm.
1065	<0·0001	$1\cdot1\times10^{-12}$	1425	0·0005	$3\cdot4\times10^{-11}$
1065	0·004	$4\cdot3\times10^{-12}$	1425	0·002	$3\cdot5\times10^{-11}$
1210	<0·0001	$2\cdot2\times10^{-12}$	1425	0·004	$6\cdot9\times10^{-11}$
1210	0·004	$5\cdot8\times10^{-12}$	1425	0·007	$1\cdot5\times10^{-10}$
1210	0·008	$1\cdot9\times10^{-11}$	1425	0·011	$3\cdot2\times10^{-10}$
1280	<0·0001	$3\cdot1\times10^{-12}$	1550	0·004	$1\cdot6\times10^{-10}$
1280	0·0015	$3\cdot4\times10^{-12}$	1570	0·0006	$1\cdot7\times10^{-10}$
1280	0·004	$1\cdot1\times10^{-11}$	1570	0·011	$9\cdot2\times10^{-10}$
1280	0·006	$2\cdot5\times10^{-11}$	1780	0·004	$6\cdot9\times10^{-10}$
1280	0·021	$1\cdot0\times10^{-10}$	1790	0·001	$6\cdot9\times10^{-10}$
1425	0·00015	$2\cdot7\times10^{-11}$	1790	0·0075	$1\cdot9\times10^{-9}$
1425	0·00025	$3\cdot2\times10^{-11}$	1830	0·004	$3\cdot1\times10^{-9}$

These values are plotted in the form of curves in fig. 5, the logarithmic scale of ordinates used being twice those taken in the preceding cases.

Table V.—Argon. Potential 210–220 volts.

Temp.	Pressure.	Ionisation.	Temp.	Pressure.	Ionisation.
°	mm.	amp. per sq. cm.	°	mm.	amp. per sq. cm.
1270	0·009	$4\cdot3\times10^{-11}$	1460	0·0008	$3\cdot4\times10^{-11}$
1270	0·012	$5\cdot1\times10^{-11}$	1460	0·009	$7\cdot8\times10^{-11}$
1280	0·002	$3\cdot5\times10^{-12}$	1570	0·0003	$1\cdot3\times10^{-10}$
1290	<0·0001	$1\cdot7\times10^{-12}$	1590	0·001	$2\cdot0\times10^{-10}$
1290	0·003	$6\cdot7\times10^{-12}$	1590	0·002	$2\cdot5\times10^{-10}$
1340	0·0001	$1\cdot0\times10^{-11}$	1590	0·009	$3\cdot8\times10^{-10}$
1340	0·0003	$1\cdot0\times10^{-11}$	1590	0·012	$6\cdot15\times10^{-10}$
1340	0·009	$5\cdot9\times10^{-11}$	1800	0·0025	$6\cdot7\times10^{-10}$
1340	0·012	$6\cdot9\times10^{-11}$	1815	0·003	$7\cdot7\times10^{-10}$
1440	0·012	$1\cdot5\times10^{-10}$	1860	0·005	$3\cdot1\times10^{-9}$

These values are represented in the form of curves in fig. 6, the logarithmic scale of ordinates being the same as in the case of helium.

In the case of all figures given in the above tables the readings represent the results obtained when the ionisation current had become stationary After a change of pressure of gas in the vessel, an appreciable interval was usually necessary before the ionisation assumed a constant value. This time effect is shown in experiments tabulated below.

The important result is at once clear from these tables, that whereas with the gases which are known to react with carbon, a very large effect is exerted by the pressure of the gas on the ionisation, while with the inert gases the ionisation shows comparatively very little change over a large range of pressure, and gives values of a much smaller order of magnitude than the other gases.

In the case of all gases, at the minimum pressures, the ionisation converges to a limiting value determined only by the temperature. This is probably due to the influence of residual impurities retained by the carbon.

Table VI.—Change of Ionisation after Change of Pressure of Gas.

1. Carbon Monoxide admitted to the evacuated vessel.

Temperature of carbon, 1180°. Pressure of gas admitted, 0·005 mm.		Temperature of carbon, 1280°. Pressure of gas admitted, 0·003 mm.	
Time.	Ionisation.	Time.	Ionisation.
	amp. per sq. cm.		amp. per sq. cm.
0·25 min.	2·1 × 10^{-11}	0·25 min.	1·3 × 10^{-11}
1·0 "	1·5 × 10^{-10}	0·5 "	7·0 × 10^{-11}
1·5 "	1·9 × 10^{-10}	1·0 "	6·0 × 10^{-10}
2·0 "	2·4 × 10^{-10}	2·0 "	1·0 × 10^{-9}
3·0 "	2·8 × 10^{-10}	3·5 "	1·5 × 10^{-9}

2. Carbon Dioxide.

Temperature, 1160°. Pressure, 0·008 mm.		Temperature, 1270°. Pressure, 0·003 mm.	
Time.	Ionisation.	Time.	Ionisation.
	amp. per sq. cm.		amp. per sq. cm.
30 secs.	7·0 × 10^{-12}	5 secs.	1·1 × 10^{-11}
1 min.	7·0 × 10^{-11}	15 "	8·8 × 10^{-11}
1½ "	1·5 × 10^{-8}	1 min.	1·4 × 10^{-10}
2½ "	2·3 × 10^{-8}	1½ "	4·4 × 10^{-10}
3 "	2·3 × 10^{-8}	3 "	6·5 × 10^{-10}
		4 "	2·1 × 10^{-9}
		5 "	3·1 × 10^{-7}
		6 "	3·1 × 10^{-7}

Ionisation on Reduction of Pressure in above Experiment at 1160°.

Time.	Pressure.	Ionisation.
mins.	mm.	amp. per sq. cm.
0	0·008	2·3 × 10^{-8}
1½	0·001	9·9 × 10^{-9}
2½	0·0005	9·9 × 10^{-9}
3½	$<$0·0001	9·9 × 10^{-9}
Temperature raised to 1350° and lowered to 1160°.		
	$<$0·0001	1·5 × 10^{-12}

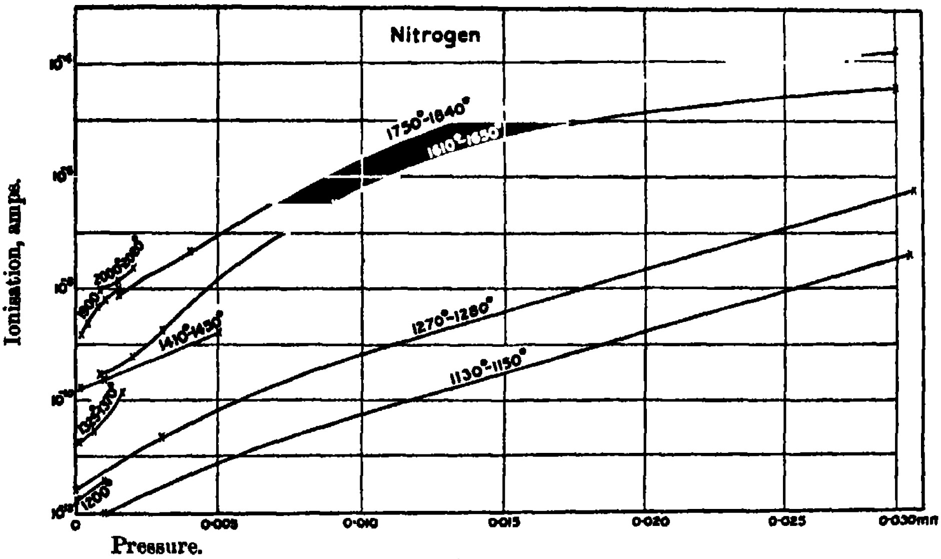
Nitrogen
Ionisation, amps.
1750°-1840°
1610°-1650°
1800°
2000°-2080°
1410°-1450°
1320°-1370°
1270°-1280°
1130°-1150°
1200°
0
0·005
0·010
0·015
0·020
0·025
0·030mm
Pressure.

FIG. 2.

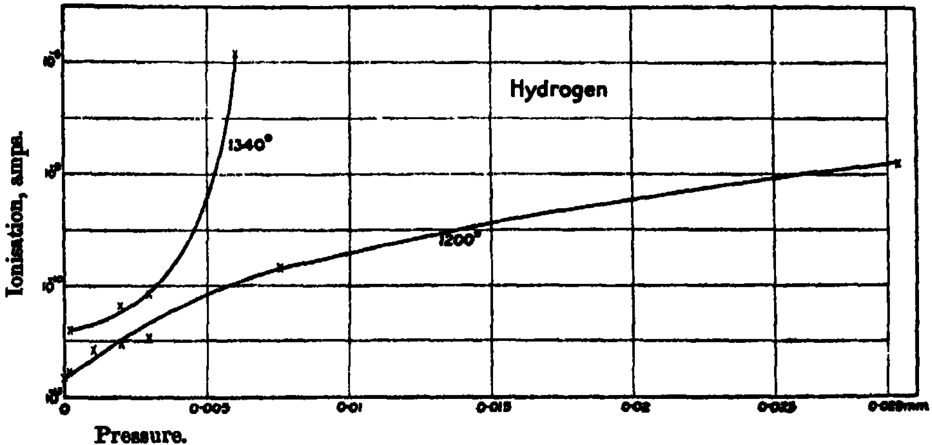
Hydrogen
Ionisation, amps.
1340°
1200°
0
0·005
0·01
0·015
0·02
0·025
0·029mm
Pressure.

FIG. 3.

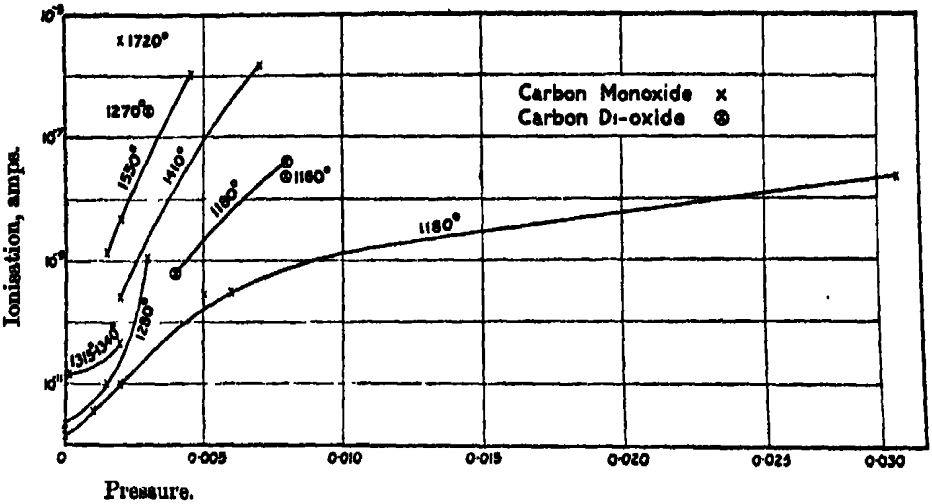
10^{-5}
10^{-7}
10^{-9}
10^{-11}
Ionisation, amps.
× 1720°
1270° ⊗
1550°
1410°
1180°
⊗ 1160°
1180°
1280°
1315°-1340°
Carbon Monoxide ×
Carbon Di-oxide ⊗
0
0·005
0·010
0·015
0·020
0·025
0·030
Pressure.

Fig. 4.

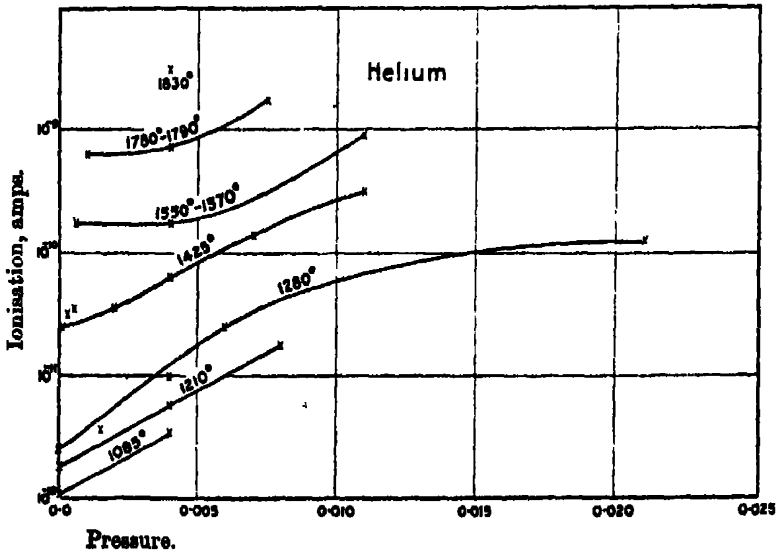
Helium
10^{-9}
10^{-10}
10^{-11}
10^{-12}
Ionisation, amps.
1830°
1780°-1790°
1550°-1570°
1425°
1280°
1210°
1085°
0·0
0·005
0·010
0·015
0·020
0·025
Pressure.

Fig. 5.

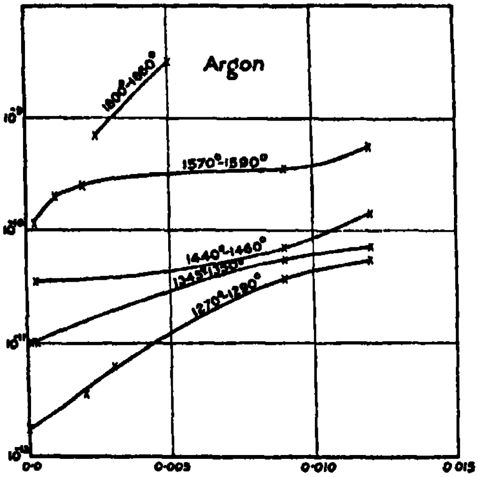

Fig. 6.

Discussion of Results.

A. *Relation between Ionisation and Pressure.*

It is seen from Table VI above that, on admitting gas at a higher pressure during an experiment, a certain interval was necessary before the maximum of ionisation was attained. With the inert gases (helium and argon), which gave the lowest ionisation, this time effect could not be observed, but with the other gases it increased in proportion to their final ionisation current. Thus, at about 1200°, hydrogen gave a maximum value in about 30 seconds, carbon monoxide in about 3 minutes, and carbon dioxide not until after 5 minutes.

If equilibrium was reached at any given pressure, and the pressure was then lowered, at first only a slight decrease in the ionisation followed, and finally, in some cases, the current would suddenly fall to a lower value. The high ionisation obtained at low pressures could also, in some cases, be suddenly lowered by momentarily interrupting the potential applied to the circuit. In many cases, however, the reduction could only be brought about by taking the temperature considerably higher—while the pressure was low—and then lowering again. This time lag or hysteresis in the ionisation has been observed by other workers, and it is quite apparent from these results that it is caused mainly by an occlusion of the gas in the carbon. The gas is only very slowly evolved on heating, and probably it cannot be entirely eliminated.

Readings taken after a reduction of pressure during the experiments have not been entered in the above Tables (I to V) on account of their uncertain value.

B. *Influence of Potential on Ionisation Currents.*

It is seen that in the experiments conducted at low pressures, the potential difference used to collect the ionisation played a comparatively unimportant *rôle.* If the fundamental ionisation arising from the carbon was largely increased by ionisation by collision in the gas, a very large change of current with potential would have been expected. Hence the great differences observed when using different gases cannot be explained by the known differences in ionic mobilities.

C. *Effect of Different Gases on the Magnitude of the Ionisation.*

The results of the measurements with different gases given in Tables I–V show that the ionisation from carbon increases in these cases in the following order:—

$\left.\begin{array}{l}\text{Helium,}\\ \text{Argon,}\end{array}\right\}$ nitrogen, hydrogen, carbon monoxide, and carbon dioxide.

This order is the same as for the known chemical activity between carbon and these gases.

While the first two are chemically inert, nitrogen reacts to a small degree to form cyanogen,[*] and with hydrogen to form small quantities of methane, ethylene, and acetylene,[†] while carbon monoxide gives a small quantity of carbon dioxide and carbon,[‡] and carbon dioxide reacts rapidly to give carbon monoxide.

With the inert gases the increase of ionisation with pressure is seen to be very slight indeed when compared with the active gases. It is seen from the curves (figs. 2 to 6) that the ionisation does not converge to zero at the lowest pressures, but rather assumes a constant value for each temperature. This is what would be expected in the light of the above phenomena of absorption. At the lowest pressures the amount of gas held in the carbon would always appear to correspond to a higher pressure on the outside, and it was indeed found that the higher the temperature to which the carbon had been previously heated, while keeping the pressure constant—and thus the more completely the occluded gas had been driven out—the lower the final value to which the ionisation was reduced at that pressure. By repeatedly admitting and withdrawing one of the inert gases, the ionisation from the heated carbon was also considerably lowered, but could not be reduced beyond a certain limit, as would be expected from the impossibility of excluding completely extraneous gas when working at the high temperatures.

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[*] H. v. Wartenberg, 'Zeit. f. Anorg. Chem.,' 1907, p. 52, pp. 299–315; Smith and Hutton, 'Amer. Electroch. Soc. Trans.,' 1908, vol. 13, pp. 359–365.

[†] Pring and Fairlie, 'Chem. Soc. Trans.,' 1912, vol. 101, p. 91.

[‡] Rhead and Wheeler, 'Chem. Soc. Trans.,' 1910, vol. 98, p. 2178.

In fig. 7 curves are plotted to show the ionisation produced by the different gases when at a constant pressure of 0·005 mm. The ordinates are expressed in ampères multiplied by 10^{-12} and the abscissæ represent the temperatures.

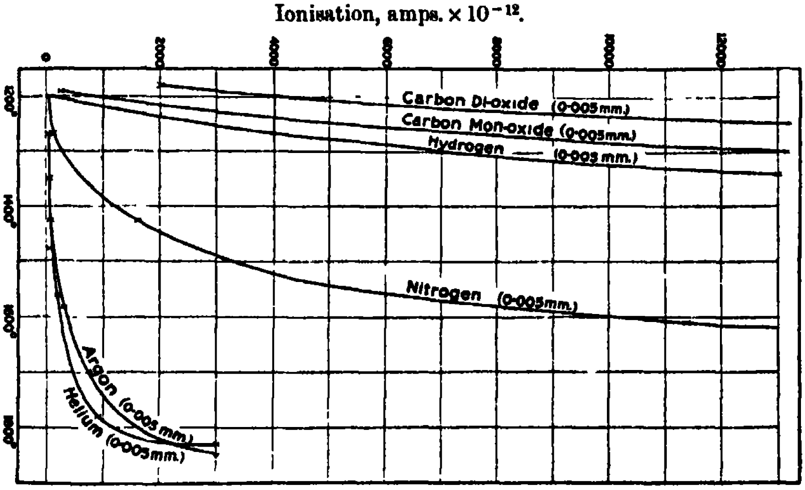

Fig. 7.

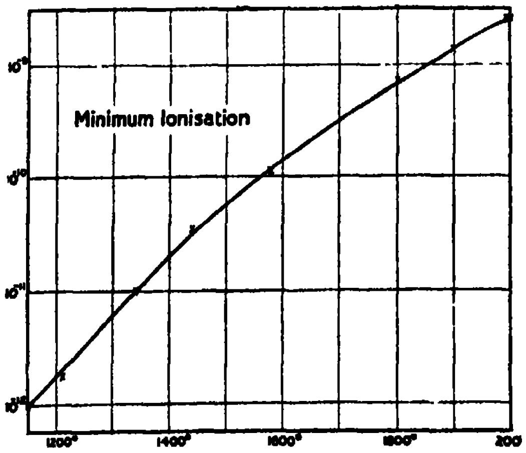

Fig. 8.

Fig. 8 shows, in the form of a curve, the minimum ionisation values obtained from the carbon at the lowest pressures used. The ordinates here represent the logarithm of the ionisation and the abscissæ the temperatures.

The minimum current for 1 sq. cm. surface of carbon is seen to be $1 \cdot 7 \times 10^{-13}$ at 1200°, and $8 \cdot 5 \times 10^{-9}$ at 2025°. These values are respectively about 10^7 and 10^{14} times smaller than those originally estimated by Richardson (*loc. cit.*), and which formed the basis of the theory of thermionic emissivity, and are about 10^5 times smaller than the values recalculated by Richardson (*loc. cit.*) after the revision of the constants of his formula.

Summary and Conclusions.

The ionisation produced by carbon at high temperatures, which hitherto has been generally held to be mainly due to direct electronic emission, was found in some earlier work to be dependent to a very high degree on the presence of gas and other impurities in contact with the carbon. The conclusion then drawn, that the large currents hitherto observed were derived from some reaction between the carbon and the gas, has been confirmed in the present work.

It has been shown that a still further large reduction in the ionisation is brought about by eliminating further the absorbed gases from the carbon.

By admitting known amounts of different pure gases to the carbon the ionisation produced was found to be directly proportional to the known chemical activity of these gases. The progress of absorption of the gas by the carbon and its evolution could, moreover, be traced by the ionisation currents.

It is clear from these results that the thermal ionisation ordinarily observed with carbon is to be attributed to chemical reaction between the carbon and the surrounding gas.

While it is difficult to prove definitely that there is no electronic emission from the heated carbon itself, it is obvious that it is exceedingly small compared with ionisation which can be attributed to ordinary chemical change. The small residual currents which are observed in high vacua after prolonged heating are not greater than would be anticipated when taking into account the great difficulty of removing the last traces of gas.

I wish to thank Prof. Rutherford for the kind interest he has taken in the progress of this work.

On the Refraction and Dispersion of Gaseous Nitrogen Peroxide.

By Clive Cuthbertson, Fellow of University College, London, and
Maude Cuthbertson.

(Communicated by Alfred W. Porter, F.R.S. Received July 29, 1913.)

The study of the refraction and dispersion of gaseous nitrogen peroxide (NO_2, N_2O_4) is specially interesting, owing to the opportunity it affords for observing the changes which accompany the polymerisation of the molecule. No previous determinations are recorded in the usual books of reference.

Preparation.

The gas which we used was prepared by heating pure lead nitrate, which had previously been ground to fine powder and heated for two hours to 150° C. to expel moisture. It was condensed in a bulb, and quantities of about a cubic centimetre of the liquid were sealed off in glass tubes which were broken *in vacuo* in a dry bulb containing P_2O_5. Taps were usually lubricated with metaphosphoric acid, but in some cases with a mixture of pure paraffin and vaseline, which was not appreciably attacked by the gas.

Apparatus and Procedure.

For the determination of refractive indices Jamin's refractometer was used. The bulb containing the liquid NO_2 was connected with the refractometer tube by a tap. Another tap connected with a manometer, consisting of two U-tubes in series, the first containing oil and the second mercury. A long capillary separated the oil from the tap which led to the NO_2.

In a measurement of the refraction the liquid NO_2 was first cooled to $-80°$ C., at which temperature its vapour pressure is negligible, and the whole apparatus was evacuated with a Töpler pump, through tubes containing soda-lime and potash and P_2O_5, till the difference of pressure shown by the manometer corresponded with the barometric height.

The manometer tap was then closed and the liquid allowed to warm, while the observer counted the interference bands which passed the cross-wire as the vapour flowed into the refractometer tube. When a convenient number had passed, the tap connecting the bulb of NO_2 was closed, and dry air was admitted into the manometer till the pressure nearly equalled that of the nitrogen peroxide. The manometer tap was then opened, and the difference between the pressure of the atmosphere and that of the gas was read.

The barometric height was again taken, the temperature observed, and the number of bands noted.

The density of the gas present in the refractometer tube was determined by means of a density bulb connected with it in parallel, and immersed in the same water-bath.

Light.

Owing to the strong absorption of the vapour it was found impossible to use the mercury green line ($\lambda = 5460$) for measurements of refraction. For this purpose we used red light ($\lambda = 6438$) obtained by means of a fixed-deviation spectroscope, fitted with an adjustable slit at the eye end, which sifted out a band of light not exceeding 10 Å.U. in width. Even with this red light the maximum number of bands which could be counted when the vapour contained 96 per cent. of NO_2 was only about 80, so that great accuracy was not attainable.

Reduction of Observations.

Our object is to compare the refractive and dispersive powers of the molecules of NO_2 and N_2O_4 respectively, and their relation to those of nitrogen and oxygen. It is, therefore, necessary to reduce the refractivities experimentally observed at various temperatures and pressures to the same standard conditions as those under which the refractivities of the permanent gases are usually expressed. These are, of course, that the temperature and pressure of the gas should be 0° C. and 760 mm. But in dealing with substances which are not perfect gases, it is desirable to substitute for these conditions the real standard which they are meant to define, viz., that the number of molecules of the gas present in unit volume should equal the number of molecules present in unit volume of a permanent gas, *e.g.* oxygen, at 0° C. and 760 mm. pressure.

In the present case the pressure and temperature of the gas were observed, and it was assumed, for the purpose of the reduction, that each constituent (*i.e.* NO_2 and N_2O_4) behaved as a perfect gas, and that the mixture remained of the same composition. Upon these assumptions the reduced refractivity, which we shall denote by $(\mu_\lambda - 1)_{0\cdot76}$, is given by

$$(\mu_\lambda - 1)_{0\cdot76} = \frac{N\lambda}{L}\frac{t}{273}\frac{76}{p},$$

where N is the number of interference bands, L the length of the tube, t and p the temperature and pressure of the experiment.

The observed density* of the gas was reduced in the same manner. If d denotes the observed density (grammes per litre) and D the reduced density,

$$D = d \frac{t}{273} \frac{76}{p}.$$

The standard density for each constituent was obtained from the following figures :—

						Grammes.
	Weight of	1	litre of	nitrogen	at 0° C. and 76 cm.	1·25718
	„	½	„	„	„	0·62859
	„	1	„	oxygen	„	1·42952
Hence	„	1	„	NO_2	„	2·05811
and	„	1	„	N_2O_4	„	4·11622

We have thus obtained a reduced refractivity and a reduced density. The former expresses the refractivity which would be given at 0° C. by a gaseous mixture in which the proportions of molecules of NO_2 and N_2O_4 were those which exist at the temperature and pressure of the experiment, and for which the density was such that the number of molecules present per cubic centimetre was equal to the number present in unit volume of oxygen at 0° C. and 760. The latter gives us the weight of unit volume of the gaseous mixture under the same conditions.

Assuming the additive law to hold good for the gaseous mixture, it is evident that if we plot the reduced refractivities against the reduced densities, we should obtain a straight line. The values of the reduced refractivities which correspond with the standard densities of NO_2 and N_2O_4 given above will be the refractivities of NO_2 and N_2O_4 under the standard conditions.

Table I gives the results of ten experiments on the refraction.

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* It may be asked why we did not use the observations of E. and L. Natanson on the connection between the density, temperature and pressure of NO_2 ('Wied. Ann.,' vol. 24, p. 445, and vol. 27, p. 606). These were determined from observations at nine temperatures nearly all above 20° C., and at the low temperatures and pressures which it was necessary for us to use in order to obtain a large percentage of N_2O_4, the discrepancies between their observations and the values calculated from Willard Gibbs' formula are so great that it was impossible to use them for the calculation of the density at intermediate temperatures and pressures.

Schreber ('Zeit. Phys. Chem.,' 1897, vol. 24, p. 660) has analysed the observations of the brothers Natanson, and gives a formula from which the dissociation constant can be calculated at any temperature and pressure. Our first series of experiments was based on the use of this formula, but after three months' work it was found that it, too, is untrustworthy at low temperatures.

Table I.—Refractivity of Gaseous Nitrogen Peroxide ($\lambda = 6438$).

No. of expt.	Length of tubes.	Temperature (absolute).	Pressure.	No. of bands for $\lambda = 6438$.	Refractivity $(\mu-1)10^7$. Experimental $\left(\frac{N\lambda}{L}\right)$.	Reduced $\left(\frac{N\lambda}{L}\cdot\frac{t}{273}\cdot\frac{76}{p}\right)$.	Density. Experimental. $d = \frac{\text{grm.}}{\text{litre}}$.	Reduced. $D = \frac{\text{grm.}}{\text{litre}}\cdot\frac{t}{273}\cdot\frac{76}{p}$.
	mm.		mm.					
5	197·78	273	180·4	71·35	2323	9783	0·8625	3·634
8	197·78	273	176·9	69·7	2269	9748	0·8458	3·632
3	197·78	270	190·9	71·6	2331	9483	0·8663	3·528
4	197·78	283·6	187·35	66·6	2168	9139	0·8086	3·408
1	197·78	288·9	174·3	57·45	1870	8629	0·7029	3·240
9	197·78	299·6	237·9	70·0	2279	7990	0·8660	3·037
6	197·78	303	196·5	51·7	1683	7225	0·6455	2·771
7	197·78	311	189·5	47·25	1538	7027	0·5944	2·716
11	997·86	308·9	55·3	60·4	389·7	6059	0·1522	2·367
12	997·86	342·9	61·15	49·7	221·2	5006	0·1314	2·052

In fig. 1 the values for the reduced refractivity are plotted against the corresponding values for the reduced density.*

The points fall on a straight line which cuts the ordinate whose abscissa is 2·0581 at the point 508·7, and the ordinate whose abscissa is 4·1162 at the point 1123. The constants, calculated by the method of least squares, give the following equation to this line:—

$$10^7(\mu-1)_{0\cdot76} = 2983\cdot4\,D - 1053\cdot3.$$

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* It is, perhaps, not obvious why we should not obtain a similar straight line by plotting the experimental values of the refractivity and density instead of the reduced, since the latter are both derived from the former by multiplying by the same factor. But this is not so.

In any one gaseous mixture let there be n_1 molecules of NO_2 and n_2 of N_2O_4. Let the refractivities of one molecule of NO_2 and one molecule of N_2O_4 be denoted by (μ_1-1) and (μ_2-1) respectively, and that of the mixture by $(\mu_{12}-1)$; and let the molecular weights of the two constituents be M_1, M_2.

We have $$(\mu_{12}-1) = n_1(\mu_1-1)+n_2(\mu_2-1), \qquad \text{i}$$

and, assuming the perfect gas law for each constituent,

$$p = (n_1+n_2)Rt, \qquad \text{i}$$

also $$d = n_1M_1+n_2M_2,$$

whence $$(\mu_{12}-1) = \frac{p}{Rt}\,\frac{[(\mu_1-1)M_2-(\mu_2-1)M_1]+d(\mu_2-\mu_1)}{M_2-M_1}.$$

Multiplying by $\frac{t}{p}$ we have

$$(\mu_{12}-1)\frac{t}{p} = \frac{1}{R(M_2-M_1)}[(\mu_1-1)M_2-(\mu_2-1)M_1]+\frac{dt}{p}\,\frac{(\mu_2-\mu_1)}{M_2-M_1},$$

a linear equation between the reduced refractivity and reduced density.

The discrepancies between the calculated and observed values of the refractivity are all less than 0·35 per cent., except in the last two experiments, where they are +0·85 and −1·2 respectively. This was to be expected, owing to the low pressure and high temperature of the experiments, which increases the difficulty of determining the density.

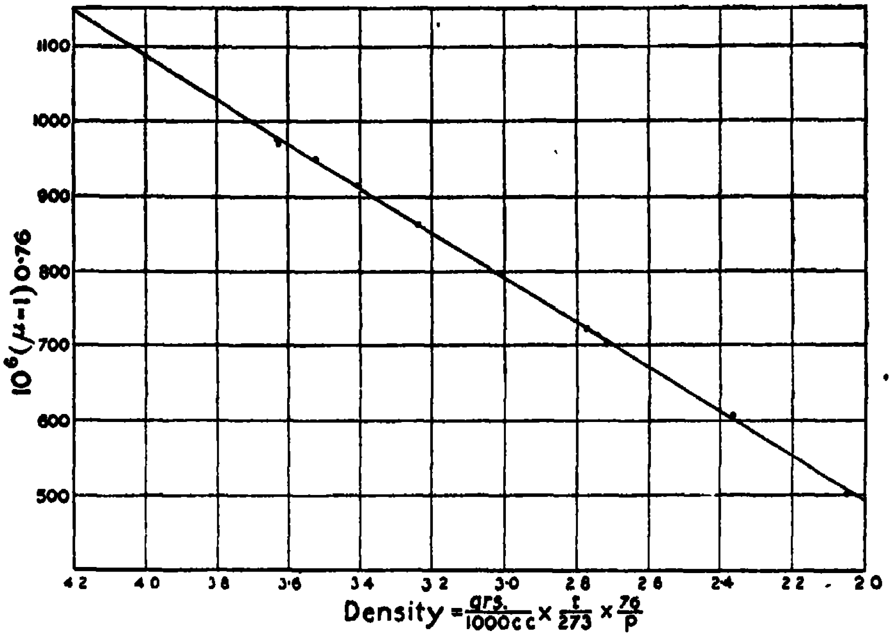

FIG. 1.—Reduced refractivity of nitrogen peroxide plotted against reduced density.

Hence, finally, we obtain as the reduced refractivity of pure NO_2 for $\lambda = 6438$

$$10^7(\mu-1)_{0\cdot76} = 0\cdot0005087,$$

and for pure N_2O_4 $$10^7(\mu-1)_{0\cdot76} = 0\cdot001123.$$

It thus appears that the refractivity of a molecule of N_2O_4 exceeds that of two molecules of NO_2 by about 10½ per cent.

In order to check this result we tried the experiment of operating with a constant density of gas at different temperatures. The gas was admitted to the tube in the usual way, and the pressure, temperature, and bands read. The refractometer tube was then sealed off with as short a side tube as possible, and the tubes were heated and cooled in a water-bath, while the variation of the position of the bands was observed. The results were as follows :—

Temperature.	Pressure.	Bands.
274·1	37·74	62·45
290	Not observed	60·8
303	"	60·2
331·5	"	57·4
344	"	57·3

As the temperature was raised the proportion of molecules of NO_2 increased, while the density of the gas remained constant. The diminution of the retardation of light under these circumstances, which is shown by the retrogression of the bands, proves that the refractivity per molecule of NO_2 is less than that of N_2O_4. The rate of diminution is rather faster than we should expect from the results of the main experiment; but the accuracy of this subsidiary form of experiment is seriously affected by "drift" or "end effects" owing to the changes of temperature, and the weight to be attributed to it, as a quantitative experiment, is small.

Relation to Refractivities of Nitrogen and Oxygen.

We have recently shown that the refractivities of ammonia, nitric oxide and nitrous oxide are greater than the sum of the refractivities of the elements which compose them by 3·6, 3, and 16·3 per cent. respectively.[*]

Nitrogen peroxide exhibits the same phenomenon. The additive value for NO_2 is found from

$$(\mu-1)_{N_2} = 0·000299.$$

Half of this is $0·0001495,$

and $(\mu-1)_{O_2} = 0·000271.$

The sum is $0·0004205,$

while the experimental value is 0·000509, an increase of 21 per cent.

DISPERSION.

Procedure.

Measurements of the dispersion are limited, by the absorption, to the red and green, and even in this region trustworthy values would be difficult to obtain were it not for the enormous dispersive power of the molecule of NO_2. In order to trace the shape of the dispersion curve as it passes through the absorption bands it was necessary to abandon the monochromatic sources of light which are available when a gas is transparent to the whole spectrum, and to do the best which is possible with a narrow section of the spectrum of white light. In this case the source was a Nernst lamp. The fixed-deviation spectroscope was fitted with an adjustable slit at the eye end, and the two slits were narrowed till the beam which passed through the second slit did not exceed 10 Å.U. in breadth. The apparatus was evacuated and the optical paths of the two beams equalised by means of the compensator, so that no movement was seen in the position of the interference bands as the light was continuously changed from λ 6708 to λ 5461. Gas was now admitted till a convenient number of bands (λ 6438) had passed, when the supply was cut off. The compensator was then altered till the same number of bands had passed in the opposite direction. If the wave-length drum is now rotated any change in the position of the band is due to the difference of dispersive powers of glass and gas.*

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[*] 'Phil. Mag.,' April, 1913, p. 592.

Three sets of experiments were made; the first, at the lowest temperature and highest pressure which could conveniently be used, so as to obtain the greatest proportion of molecules of N_2O_4. The reduced density of this mixture was about 3·63, and the proportion of molecules of N_2O_4 present was 76·5 per 100 molecules.

At an intermediate temperature and pressure a single experiment was made on gas containing 48 per cent. of molecules of N_2O_4.

The third set was made at the highest temperature and lowest pressure convenient, on gas containing approximately 4 per cent. of molecules of N_2O_4 and 96 per cent. of NO_2.

The results are shown graphically in fig. 2 (1, 2, 3).

In the first set of experiments, in which the proportion of NO_2 was small, the curve could be traced throughout its whole length as far as $\lambda = 5500$. It is comparatively smooth, but shows clearly the characteristic rise and relative fall on passing through each region of absorption.

In fig. 2 (2) is shown the curve obtained with 52 per cent. NO_2, but the final density of the gas was so great that much light was absorbed, and only six points on the curve could be obtained, intermediate parts of the spectrum being obliterated.

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* The compensator was of special design and retards light of all wave-lengths equally except so far as dispersion affects them. It consisted of two pairs of wedge-shaped pieces of glass, with their thick ends opposed, mounted vertically in a metal frame with their exterior surfaces at right angles to the beam of light.

Three of the wedges are fixed. The fourth is movable vertically by means of a screw, and is mounted so that the distance between the interior surfaces remains constant. Each of the two beams of light passes through one pair of wedges, which are optically equivalent to a plane parallel sheet of glass. By screwing the movable wedge up or down, the path of one of the two beams is accelerated or retarded, and all wave-lengths equally, except so far as dispersion affects them.

Fig. 2 (3) gives the curve obtained from the third set of experiments, when 96 per cent. of NO_2 was present. It shows the increased size of the humps on the curve due to the increased percentage of NO_2, and gives a fair idea of the position of their maxima and minima. But farther than this the accuracy of this series cannot be trusted. In order to obtain readings between $\lambda\lambda$ 6000 and 5600, it was necessary to reduce the number of bands to 17, and even to 13, and, under these conditions, an error of 1/30 of an interference band was equivalent to an error of 0·004 in the value of the refractivity.

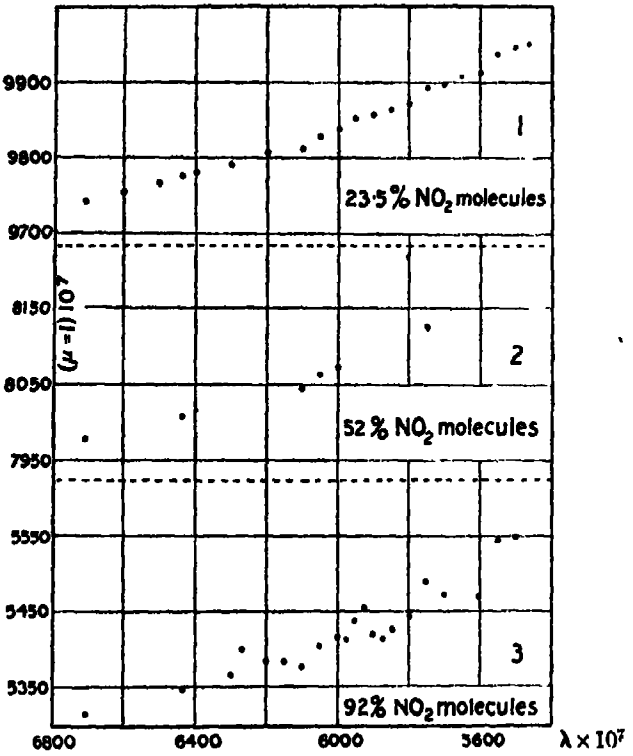

Fig. 2.—Dispersion of nitrogen peroxide.

In the figure the three curves have about the same inclination to the horizontal. But, since the refractivity diminishes as we pass from (1) to (3), the dispersive power $(\mu_1-\mu_2)/(\mu_1-1)$ increases in the same order and proportion.

Remarks.

It is well known that, with sufficient dispersion, and at low temperatures, the absorption bands of NO_2 are seen to consist of fine lines, which blend into a band as the temperature is raised,* and, no doubt, if it were possible to trace our dispersion curve from line to line, a series of small maxima would be shown. Our apparatus is not capable of indicating these microscopic changes, but only records the general effect in passing through a region of absorption.

The most interesting question raised by these observations is the cause of the increase of refractivity which accompanies polymerisation, coupled with the decrease of dispersive power. It is much to be desired that measurements of the refractivity should be supplemented by accurate observations of the position of the absorption bands in the infra-red and ultra-violet for each constituent separately. So far as we can discover, no one has attempted this. Hartley† records that the gas is transparent between λλ 321 and 238, but this appears to be all that is known.

We are much indebted to the Royal Society for a grant in aid of this work.

Summary.

The results given above may be summarised as follows:—

1. The refractivity of pure NO_2 for $\lambda = 6438$, reduced to standard conditions by the formula $(\mu-1)_{0\cdot76} = \frac{N\lambda}{L}\frac{t}{273}\frac{76}{p}$ is approximately 0·000509. That of pure N_2O_4 is 0·001123, so that the effect of polymerisation is to increase the refractivity by about 10½ per cent.

2. The refractivity of a molecule of NO_2 is greater than those of the elements of which it is composed by 21 per cent.

3. The dispersive power of a molecule of NO_2 in the red and green is considerably greater than that of a molecule of N_2O_4.

* Liveing and Dewar, 'Roy. Soc. Proc.,' vol. 46, p. 222.

† Hartley, 'Chem. Soc. Journ.,' 1881, vol. 39, p. 111.

On the Diffraction of Light by Particles Comparable with the Wave-length.

By B. A. Keen, B.Sc., Physics Research Scholar, and Alfred W. Porter, F.R.S., Fellow of University College, University of London.

(Received October 1,—Read November 27, 1913.)

This research was undertaken to investigate an effect first noticed by one of us (A. W. P.) when experimenting with the light scattered by suspensions of finely divided sulphur. These were obtained, in the well-known way, by depositing sulphur from a solution of thiosulphate of soda by means of a weak acid. When such a suspension is placed in the path of a beam from an arc lamp focussed on a screen, the image of the carbon is usually red, of greater or less depth according to the size and number of the diffracting particles. The production of this red colour has been satisfactorily explained by Lord Rayleigh* as due to the selective scattering of blue light by particles which are small compared with the wave-length of the light.

One of us noticed, however, that if time be given for the particles to increase in size (and possibly in number also) the solution after becoming nearly opaque becomes transparent again, but in this new stage an excess of *blue is transmitted*, which attains at one stage a deep indigo tint, this afterwards changing through various blue-green and green tints, to white.

This very remarkable result is in direct variance with the current theory of the action of small particles, and presents, therefore, a problem requiring investigation. While making quantitative measurements upon it we found that analogous phenomena had been observed previously, though no thorough investigation had been undertaken to explain the effect observed.

For example Captain Abney,† in connection with his preparation of a photographic plate which would be sensitive to the infra-red region, experimented with silver bromide and attempted to get it in a different molecular condition from that generally found. He says: "I need not detail the different methods of preparation of this compound in collodion that were carried out. In some cases I obtained it in a state which, when viewed by transmitted light, appeared of a sky-blue colour inclining to green, visibly absorbing the red. In this condition it (the photographic plate) was sensitive to the whole spectrum, visible and invisible."

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* 'Phil. Mag.,' 1871, vol. 41, pp. 107–120, 274–279, 447–454; 1899, vol. 43, pp. 375–384.

† 'Phil. Trans.,' 1880, Pt. II, p. 653.

Again, Walther Ritz* gives a new method of preparing the sensitive compound, giving superior results to those obtained by Abney. In the course of his directions he notes:—"Les bromures de zinc et d'ammonium sont à peu près équivalents: on peut aussi remplacer le mélange d'alcool et d'éther par de l'alcool méthylique ou de l'acétone. La transformation du bromure d'argent est donc d'ordre purement physique; elle est d'ailleurs toujours accompagnée d'une augmentation du diamètre des grains. Enfin l'émulsion a été soumise sous pression à des températures allant jusqu'à 100° pendant une heure et 40° pendant 24 heures. Il n'a cependant pas été possible de dépasser la limite donnée par Abney, le bromure devenant granuleux et se décomposant . . . . La couleur caractéristique bleue de l'émulsion d'Abney (observée par transparence) apparaît ici immédiatement et à froid."

These observations made by others are important because they show that the phenomenon is not peculiar to sulphur.

Method of Investigation.

The research consisted of measuring, at various instants after setting free the thiosulphuric acid, the transparency of the suspension to monochromatic lights of various wave-lengths. For this purpose a Hüfner spectrophotometer was employed, designed and made by Messrs. Hilger and Co. Light passing first through a fixed nicol, and then through one which can be rotated, is matched with light passing through the solution and the second nicol. On its way the light is sorted into its constituent colours by means of a constant deviation prism; the match can therefore be made for any desired colours in succession.

By trial it was found that the most suitable strengths of acid and thiosulphate to use were such that the first sign of blue *diffracted* light appeared about two minutes after mixing, at ordinary temperatures. The exact strengths used in the present work were 0·051 grm. molecule thiosulphate per litre and 0·106 grm. molecule of HCl per litre. These were approximately chemically equivalent.

It was soon found that, to obtain any concordance in the results obtained on different occasions, it was necessary to pay particular attention to temperature and also to keep the solution continually stirred. Stray light had to be excluded as far as possible, as it seriously affected the power of the eye in matching the two halves of the beam. It was also necessary to guard against fatigue of the eye in the course of an experiment. The rectangular glass cell containing the solution was of 1 cm. internal diameter. This was immersed in a larger one containing water to keep the temperature constant, while between this and the source of light another water cell was placed to act as a heat screen. As source of light a Welsbach mantle was employed. Various heat and light screens were placed where experience indicated. A thermometer was placed in the solution. Air was continually bubbled through to prevent the particles settling and to make their growth as regular as possible. The air tube was arranged so that the stream of bubbles was outside the field of view. A very steady stream of air was obtained from a toy vertical steam engine driven "backwards" by an electric motor. To prevent any considerable evaporation a glass plate was placed over the top of the small cell. The reaction was complete in about 30 minutes. At the close of an experiment the cell was cleaned with a wet plug of cotton wool to remove any adhering sulphur, thoroughly washed out with distilled water, and dried by a stream of dust-free air.

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* 'Comptes Rendus,' 1906, vol. 143, p. 167.

Two typical wave-lengths—one in the blue and the other in the red—were selected, and the complete experiment performed with one wave-length at a time. The final curves obtained (fig. 1) are each composed of three sets of readings obtained in this manner. The readings for either wave-length do not differ among themselves by more than the experimental error involved in setting the nicol.* It will be noticed that the initial portion of each curve is not

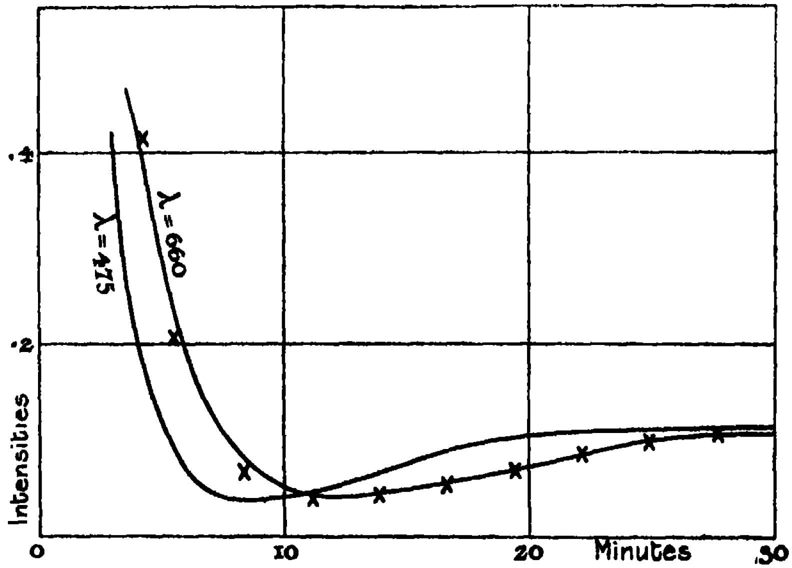

Fig. 1.

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* The experimental points have been omitted to prevent confusion. The magnitude of the experimental error, however, is slightly less than that between the values indicated by circles in fig. 2 and the mean curve drawn through them.

given. There are two reasons for this omission. In the first place very little of the light is diffracted at this early stage of the reaction, consequently the image of the source is too bright to permit of accurate comparison of the intensity of the two halves of the beam, as considerable movements of the adjustable nicol then produce no appreciable variation of intensity. The second source of error is due to the rapid rate at which the intensity changes in the early stages of the reaction, that is to say, immediately after the first pause during which no deposit is formed. This obviously makes any experimental error of more importance.

Reliable readings of this initial portion of the curve were obtained in separate experiments by interposing a colour screen in the path of that portion of the beam which passes through the solution. Although this reduced the intensity of the light in an ascertainable ratio, it made the accuracy in setting the nicol much greater, as a small movement of the nicol now

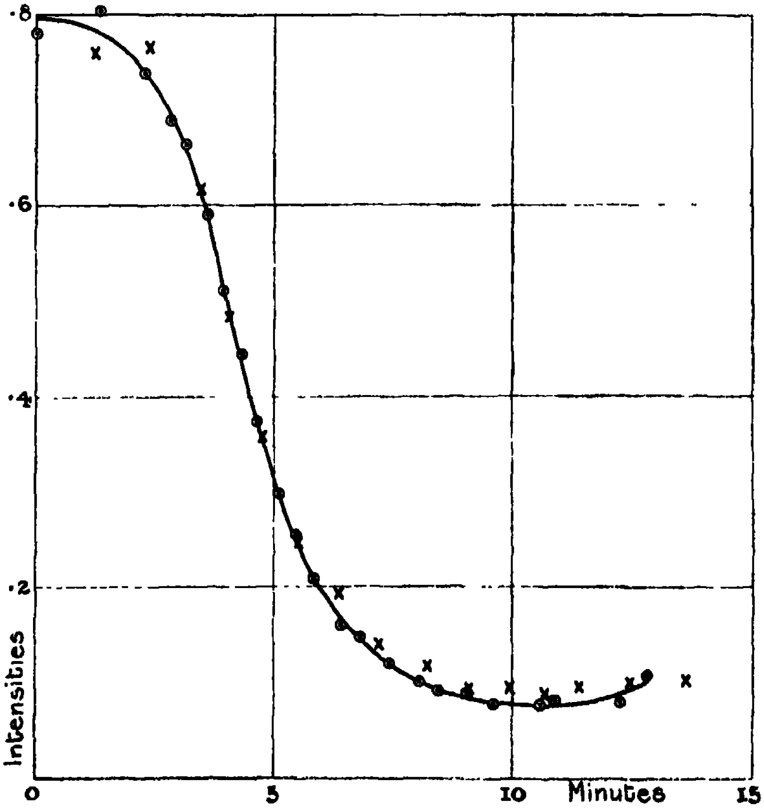

FIG. 2.—Curve showing intensity of transmitted light (λ = 535) in the early stages of the reaction.

⊙...... with colour screen } Temperature = 14° C.
×...... without colour screen

produced appreciable effect on the intensity. From these readings the corresponding intensities, had the screen been absent, were easily obtained. With the help of an assistant to read the watch, readings were taken at shorter intervals. The curve obtained is shown in fig. 2, the readings being indicated by circles. A control experiment was made without the colour screen; these readings are indicated by crosses.

As already mentioned, the growth of the particles is very sensitive to temperature changes. In fig. 3 are shown two curves to indicate this. The temperatures were adjusted by putting hot water or ice in the water-bath.

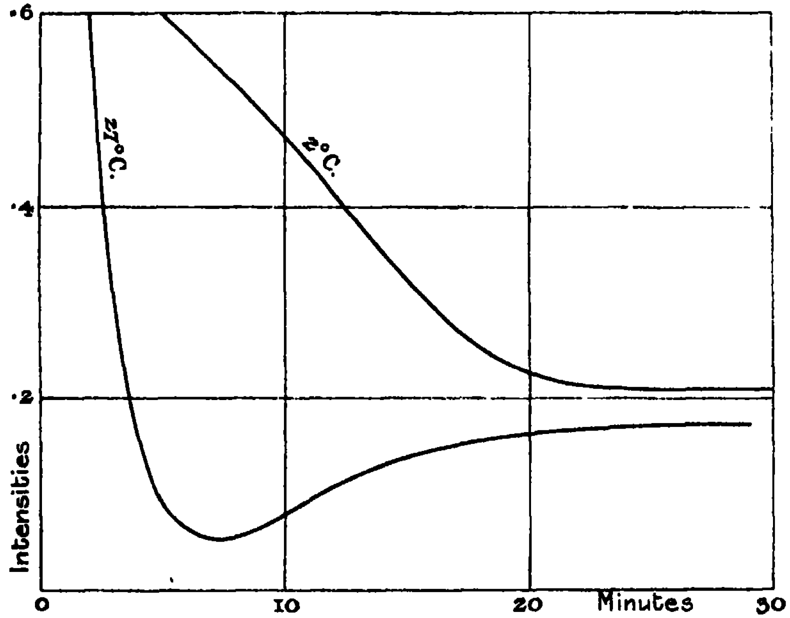

Fig. 3.—Curves showing the effect of temperature upon the reaction. λ = 660.

Naturally the temperature could not be kept very constant by this means and these curves must be regarded as qualitative only. The character of the curve is very different at the two temperatures, the observations at the lower temperature not indicating the dip which is the subject of this paper. It should be observed that the data for figs. 2 and 3 were taken with a different experimental cell from those for fig. 1.

The size of the particles was measured with the microscope when the intensity of the light passing through was a minimum, *i.e.* about 10 minutes after mixing (see fig. 1). At the end of 10 minutes a drop of the solution was placed on a slide, and further action was then stopped by neutralising the unchanged acid with ammonia. The extreme limits of variation were from 6μ to 10μ, thus indicating that the particles at this stage were considerably larger than those used by Lord Rayleigh in his experiments.* This was confirmed by repeating his experiments with solutions of the strength mentioned above. Particles of the size used by Lord Rayleigh give rise to the early portion of the curve in fig. 2.

The gradual change of the transmitted light from red through blue to white is well brought out by the curves in fig. 1. In the first stages of the reaction the intensity of the blue light falls off more rapidly than the red. At the end of about 8 minutes the blue light has reached its minimum intensity and begins to increase, while the red light is still falling to its minimum. The transmitted light—when due allowance is made for the rest of the spectrum—becomes a purple colour. After the curves cross, the blue end of the spectrum predominates, and hence we get the blue colour of the transmitted light, which gradually changes to white as the remaining rays increase in intensity. The minimum and final intensities are the same for each wave-length. The final intensity (the horizontal portion of the curves) remains constant for a considerable time and then very slowly increases, owing to the coagulation and consequent settling of the sulphur particles.

Interesting information on the rate of growth of the particles is afforded by an examination of the curves given in fig. 1. If the abscissæ of the curve for blue light are increased in the ratio of the wave-lengths, *i.e.* 660/475, the new points are very nearly coincident with the curve for red light. The points so obtained are indicated by crosses. As one would expect, the agreement is not so complete in the initial portion of the curves, but over the greater part very good agreement holds. This result shows that the transmitted intensity may be represented as a function of t/λ, where t is the time. With regard to the relation between the time and the diameter of the particles more difficulty exists. In the range through which Lord Rayleigh has extended his calculations, the intensity is a function of the diameter divided by λ. This would make the diameter of the particles increase proportionally to the time. Too much uncertainty exists in regard to the physical processes involved during the growth of the particles to devise with any confidence a theoretical value for the rate of growth. We may safely assume a practically instantaneous liberation of thiosulphuric acid, which then decomposes. If this were all, the rate of liberation of sulphur would be proportional to the undecomposed thiosulphuric acid, or

$$dx/dt = \mathrm{K}(a-x), \quad \text{and} \quad x = a(1-e^{-\mathrm{K}t}),$$

so that x itself would be a linear function of t in the early stages. But experimental evidence is in favour of the existence at first of supersaturation, which at last gives way with a sudden deposition of sulphur particles, which then grow. If we assume that the thiosulphuric acid has decomposed according to the monomolecular law throughout, and that from this stage all that is formed deposits on the particles, the same equation will still hold good for the period after the sudden deposition. But this law is too simple an account, for the process will be mainly controlled by the diffusion of supersaturated solution toward the formed particles. The amount reaching the particles may be taken as proportional to their area or to their $(\text{mass})^{2/3}$, and the equation becomes

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* 'Collected Papers,' vol. 5, p. 547; 'Roy. Soc. Proc.,' 1910, A, vol. 84, p. 25.

$$dx/dt = \mathrm{K}x^{2/3}(a-x).$$

In the early stages (for which $a-x$ can be treated as constant) this leads to

$$x^{1/3} = \text{const.} \times t,$$

so that the diameter would be a linear function of the time.

In the recent paper by Lord Rayleigh, which we have cited, interesting changes are shown to take place in the polarisation of the light as the particles increase, but there does not appear to be any indication of the phenomena with which this paper deals. We have not found it possible to modify the theoretical equations, so as to make the calculations manageable for the larger particles with which we seem chiefly to be concerned. The phenomena appear to be analogous to the different order spectra obtained with an ordinary grating. The results are published in the hope that the attention of mathematicians may be called to an interesting but very difficult region which still requires mathematical treatment.

On an Inversion Point for Liquid Carbon Dioxide in Regard to the Joule-Thomson Effect.

By Alfred W. Porter, F.R.S.

(Received October 6,—Read November 13, 1913.)

In a paper published recently in the 'Philosophical Transactions' "On the Thermal Properties of Carbonic Acid at Low Temperatures,"* Prof. C. Frewen Jenkin and Mr. D. R. Pye give, amongst other results, those obtained from a series of measurements of the Joule-Thomson effect for liquid CO_2 at various temperatures. These results are tabulated in Table V of their paper. They are of particular interest because, within the range of temperatures to which they correspond, they find an inversion point for the Joule-Thomson effect, *i.e.*, a temperature at which the effect changes over from being a cooling (at higher temperatures) to being a heating. As they themselves say: "No experiments on the Joule-Thomson effect for liquid CO_2 appear to have been published" previously; and as they admit that it is not easy to say what effect the presence of a trace of air (which was there) may have on their results, any method of testing them should prove of value. Such a test can be made by utilising the values of the specific volumes of liquid CO_2 which they give in a diagram on p. 78 of their paper.

Method of Test.

If the drop of pressure employed may be treated as a differential the Joule-Thomson effect is given by the equation

$$C_p\left(\frac{\partial T}{\partial p}\right)_{E+pv} = T\left(\frac{\partial v}{\partial T}\right)_p - v = T^2\frac{\partial}{\partial T}\cdot\left(\frac{v}{T}\right)_p.$$

The inversion point must therefore correspond to a minimum (or maximum) value of v/T.

Application of Test.

I have read off from the diagram of specific volumes the values at various pressures and temperatures and calculated the ratios v/T. These are tabulated below:—

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* 'Phil. Trans.,' 1913, A, No. 499.

$p = 400$ lb./sq. in.

t.	T.	v.	$\frac{v}{T} \times 10^5$.
° C.	Abs.		
−16·5	256·5	0·974	380
−27	246	0·933	379·3
−36	237	0·900	379·7

$p = 500$ lb./sq. in.

t.	T.	v	$\frac{v}{T} \times 10^5$
° C.	Abs.		
−4·6	268·4	1·042	380
−16·5	256·5	0·970	378·2
−27	246	0·929	377·6
−36	237	0·897	378·5

$p = 600$ lb./sq. in.

t.	T.	v.	$\frac{v}{T} \times 10^5$.
° C.	Abs.		
+5·7	278·7	1·119	401·5
−4·6	268·4	1·031	384·1
−16·5	256·5	0·967	377·1
−27	246	0·926	376·4
−36	237	0·895	377·6

All these three sets concur in giving a minimum value of v/T at a temperature not much removed from −24° C. The inversion point actually found experimentally lies between −20·7° and −31°, and by plotting their cooling effects one finds it to be at −28° C, the high pressure being between 668 and 664 lbs./sq. in., and the low pressure between 433 and 360. The mean pressure is therefore about 500 lb./sq. in. Thus, the rather remarkable result that an inversion point exists near the point found is confirmed. The result is remarkable, because it implies that liquid CO_2 is in this region behaving very nearly like a perfect gas, its volume being nearly proportional to the absolute temperature.

It may be added that 500 lb./sq. in. is about 0·46 times the critical pressure, and −28° C. is about 0·81 times the critical temperature; and that these are approximately co-ordinates of an inversion point for any van der Waals liquid.

The Diurnal Variation of Terrestrial Magnetism.

By GEORGE W. WALKER, A.R.C.Sc., M.A., F.R.S., formerly Fellow of Trinity College, Cambridge.

(Received October 15,—Read November 13, 1913.)

The diurnal variation of terrestrial magnetism has been the subject of experimental study for many years, and at a considerable number of observatories scattered all over the earth. But the co-ordination of the results, and the theoretical investigation of the physical cause or causes of the phenomena, have not made progress which seems to bear a reasonable proportion to the vast amount of observational data that has accumulated.

As far as I know, Dr. Arthur Schuster's memoirs* constitute the most inspiring and systematic attempt to reduce this matter to scientific law and order. Although I have found it convenient to depart from the method pursued by Schuster, this change of procedure was in no small degree suggested by various remarks in his memoirs.

The comparative lack of interest in the subject arises, I believe, in great measure from the difficulty (commented on by Schuster) of obtaining the experimental data in a form convenient for rational comparison. Observatories still continue to reduce their observations and to publish their results in a variety of ways, and, unless one is prepared to undertake a considerable amount of tedious arithmetical computation at the very outset, it is practically impossible to obtain a comprehensive view of what the facts are.

The Advisory Committee of Eskdalemuir Observatory recommended that the instruments should be arranged so as to record directly the geographical components of magnetic force, and, when the tabulated results for 1911 began to take definite shape, it was, perhaps, natural that I should be interested in comparing the results with those of the only other observatory which at the time also recorded the geographical components, namely, Potsdam (Seddin). The comparison, which I made in the light of Schuster's conclusions, brought out points of such interest that I was induced to attempt to collect data from other observatories as to the deduced values for the geographical components. Following Schuster, the data I desired to obtain were the Fourier coefficients in the geographical components. I confined myself to the 24-hour and the 12-hour terms, because I share the view, entertained by many of those who realise the errors that arise on the experimental and observational side, that the shorter period terms are of very doubtful accuracy.

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* 'Phil. Trans.,' 1899, vol. 180, and 1908, vol. 208.

I further confined my attention to the average yearly value, not because the seasonal variation is unimportant, but because I felt that there was a great danger of coming to grief in a multitude of facts.

The data I have been able to obtain are collected in tabular form. If they appear somewhat meagre, I would point out that I had perforce to confine my attention to observatories whose results could, without very much arithmetical labour, be put in the form desired. I hope that the information disclosed by the table will encourage others to make a contribution to it, and thus to the progress of knowledge of the phenomena.

In the table the quantities are those in the equivalent formulæ

$$a_1 \cos t + b_1 \sin t + a_2 \cos 2t + b_2 \sin 2t$$

and

$$c_1 \sin (t + \alpha_1) + c_2 \sin (2t + \alpha_2),$$

where t is the local mean time at the station and the unit of magnitude is $0{\cdot}1\,\gamma$ or 10^{-6} gauss.

From information very kindly supplied by the directors of the various observatories, the following statement may be made:—

1. Practically all days are used, not selected quiet days.

2. The original curves are not smoothed, except in the case of the V results for Pola.

3. The original curves gave records of H and D except at Eskdalemuir and Seddin, where N and W were directly recorded.

4. The hourly values are those at the exact hour, except at Seddin, where the hourly value is the estimated mean for an hour centering at the exact hour.

I need perhaps hardly say that one could wish for data obtained in precisely the same way, and that before entering on a minute arithmetical computation, all data should refer to the same year. It was soon obvious from my inquiries that one would have to wait several years before such data could be obtained.

Nevertheless, I think certain broad inferences may be drawn from the data collected in the table, and these seem to me of vital importance.

It will be convenient to review briefly the main points in Schuster's memoirs. If we grant the main proposition, that it is correct to represent the variations by a potential function, the problem may be divided into two parts:—

(1) The empirical determination of the potential function which represents the observations.

Table I.—Fourier Coefficients of the 24-hour and 12-hour Terms in the Geographical Components of Diurnal Variation of Terrestrial Variation.

Station.		Pavlovsk.	Eskdalemuir.	Wilhelmshaven.	Potsdam.		De Bilt.	Pola.		Helwan.	Bombay.	Batavia.
Lat.		59·7° N.	55·3° N.	53·5° N.	52·3° N.		52·1° N.	44·9° N.		29·9° N.	18·9° N.	6·2° S.
Long.		30·5° E.	3·2° W.	8·2° E.	13·0° E.		5·2° E.	13·9° E.		31·4° E.	72·8° E.	106·8° E.
Year.		1907.	1911.	1910.	1911.	1910.	1910.	1911.	1900 to 1909.	1909.	1904.	1908.
North.	a_1	103	107	105	96	112	118	53	60	− 63	−161	−169
	b_1	− 30	− 38	− 13	− 10	− 12	− 16	16	21	25	40	68
	c_1	107	114	105	97	113	119	56	63	− 68	−166	−182
	α_1	106°	110°	97°	96°	96°	98°	73°	71°	112°	104°	112°
	a_2	− 66	− 68	− 52	− 37	− 47	− 55	0	− 20	43	86	69
	b_2	13	8	1	− 3	3	2	− 4	5	25	− 15	− 24
	c_2	67	68	52	37	47	55	4	21	− 50	− 87	− 73
	α_2	281°	276°	271°	266°	274°	268°	179°	284°	240°	280°	290°
West.	a_1	− 85	− 76	− 97	− 77	− 93	− 96	− 30	− 92	− 66	− 22	− 9
	b_1	− 95	− 64	− 60	− 54	− 65	− 68	− 53	− 78	− 75	− 34	78
	c_1	128	99	114	95	113	118	88	121	100	41	79
	α_1	222°	230°	238°	236°	235°	235°	233°	230°	221°	213°	354°
	a_2	15	34	50	47	48	51	49	48	46	51	23
	b_2	31	64	66	66	74	70	75	92	67	27	− 84
	c_2	34	72	82	81	88	87	90	104	81	58	87
	α_2	25°	28°	37°	35°	33°	36°	33°	28°	35°	62°	165°
Vertical (down).	a_1	− 16	− 4		16	19	20	− 8	51	54	52	−140
	b_1	− 68	− 71		− 36	− 42	− 49	− 14	− 18	− 14	2	40
	c_1	70	71		39	46	53	16	54	56	52	−145
	α_1	193°	183°		156°	156°	158°	210°	110°	105°	88°	106°
	a_2	− 34	− 42		− 36	− 38	− 36	− 46	− 42	− 43	− 38	75
	b_2	− 15	− 5		− 2	− 2	− 6	13	2	17	28	43
	c_2	37	42		36	38	37	48	42	46	47	− 86
	α_2	246°	263°		266°	267°	261°	286°	273°	292°	306°	240°

(2) The theoretical investigation of the physical causes that give the potential function so determined.

These two divisions are substantially represented in Schuster's first and second memoirs. But the two divisions are not entirely independent, (1) must borrow from any hint suggested in (2), and (2) must be kept within the bounds indicated by (1).

In the first memoir, Schuster dealt with observations from the four observatories—Pavlovsk, Greenwich, Lisbon and Bombay. Observing that in the west component the Fourier terms depended substantially on the local time (a feature which is in the main confirmed by our table), he showed how the potential could be calculated. Since the west component is of the form $\delta\Omega/\sin\theta\delta\phi$, where θ is the co-latitude and ϕ the longitude, it is only necessary to get the proper expression for W in Tesseral harmonics, and then the simple integration with respect to ϕ gives, when multiplied by $\sin\theta$, the function Ω.

His conclusion reached was that the principal parts of the mean diurnal variation for the year could be expressed by a potential function of the form

$$\Omega/a = A_1 \sin\theta\cos\theta\cos(t+\alpha_1) + A_2\sin^2\theta\cos\theta\cos(2t+\alpha_2),$$

where t is the local time or the equivalent Greenwich time plus the longitude, say $(t'+\phi)$.

In the second memoir Schuster proposes to explain these terms as arising from electrical currents in the atmosphere, set up by the joint action of the permanent part of the earth's magnetic field and the mechanical oscillation of the atmosphere. Thus the barometric variation is associated with the magnetic diurnal variation. Certain formidable difficulties occur and are carefully noted by Schuster, but I need not comment on them.

In attempting to deal with the seasonal variation Schuster supposes that the conductivity of the air depends on the sun's zenith distance, and, assuming a simple and tentative expression for the conductivity, investigates the potential function that arises. The analysis is necessarily exceedingly complicated.

Let us now return to the empirical expression obtained by Schuster.

A potential of the form

$$\Omega/a = A_1\sin\theta\cos\theta\cos(t'+\phi+\alpha_1)$$

must give components to north N and to west W

$$N = +A_1\cos 2\theta\cos(t'+\phi+\alpha_1), \qquad W = -A_1\cos\theta\sin(t'+\phi+\alpha_1);$$

and again the form

$$\Omega/a = A_2\sin^2\theta\cos\theta\cos(2t'+2\phi+\alpha_2)$$

gives components

$$N = +A_2 \sin\theta\,(2-3\sin^2\theta)\cos(2t'+2\phi+\alpha_2),$$
$$W = -A_2 \sin 2\theta \sin(2t'+2\phi+\alpha_2).$$

The following Table II facilitates the comparison of the formulæ just obtained with the data collected in Table I:—

Table II.

Station.	Sin θ.	Cos θ.	Cos 2θ.	Sin 2θ.	Sin $\theta\,(2-3\sin^2\theta)$
Pavlovsk .	0·505	0·863	0·490	0·871	0·624
Eskdalemuir	0·569	0·822	0·352	0·936	0·586
Wilhelmshaven .	0·594	0·804	0·293	0·956	0·560
Potsdam	0·612	0·791	0·252	0·968	0·536
De Bilt	0·614	0 789	0·245	0·969	0·534
Pola	0·700	0·705	−0·005	1·000	0·349
Helwan	0·867	0·498	−0·504	0·864	−0·221
Bombay	0·946	0·328	−0·790	0·614	−0·648
Batavia	0·994	−0·108	−0·977	−0·214	−0·958

If now we examine the data and consider W only, then, making allowance for the fact that the data are not all for the same year, we have, I think, strong support for Schuster's expression. Batavia is, however, abnormal.

Again, taking the values for N only we have strong support for a formula of the type given by Schuster.

But clearly for any one station the values of N and W should give the same constants in the formula. This is not the case. The phase angles are not in agreement, and what is even more serious is that the observed amplitudes of the north component c_1 and c_2 are all too great as compared with the values computed from the potential function which represents the west component. The matter looks still more difficult if we compare the a_1, b_1, a_2, b_2 of N with the b_1, a_1, b_2 and a_2 of W.

I confess that the result was disconcerting, for one could see no flaw in Schuster's method, and the west values did, on the whole, depend mainly on local time. There was, of course, the possibility of a higher zonal harmonic, but this did not promise much help, and I was certainly unwilling to enter on much arithmetical computation. There remained the possibility of obtaining a function which would contribute to N without contributing largely to W. This practically meant a term depending on time from some fixed meridian, as Schuster had indicated.

After carefully studying Schuster's theory of the cause, with its ensuing complicated analysis, it appeared to me that one might reverse the whole process, that is to say, one may in a perfectly general way determine potential functions which are differentially related to opposite sides of the earth. The process may stop as soon as we get the terms which represent the data, and then we may seek for the physical meaning of the terms. In mathematical terms we start with the primary potential $1/r$. Any space derivative of this is also a potential. Thus a space derivative fixed with regard to the earth gives a contribution to the fixed part of the earth's field, while a space derivative fixed with regard to the sun gives a contribution to diurnal change.

In this simple way expressions were formed and it was found that the terms sought for could arise. I think it will be convenient to postpone consideration of the manner in which they were obtained and to give first the results.

For the 24-hour term the form of potential function at which I arrived may be written

$$\Omega = \mathrm{A}\sin\theta\cos\theta\cos(t+\alpha_1)+\mathrm{B}\sin\theta\cos(t+\alpha_2)$$
$$+\mathrm{C}(\sin^2\theta-\tfrac{2}{3})\cos(t+\phi'-\phi)+\mathrm{D}\sin^2\theta\cos(t+\phi-\phi'),$$

wherein t is the local mean time $(=t'+\phi)$ and θ, ϕ are the co-latitude and longitude of the station, while ϕ' may be regarded as the longitude of some arbitrary meridian.

Since the data do not all refer to the same year a minute numerical analysis would be out of place. Thus only round numbers were selected for the constants. By trial the following form was finally selected :—

$$10^6\,\Omega/a = (150\sin\theta\cos\theta-50\sin\theta)\cos t+(-70\sin\theta\cos\theta-10\sin\theta)\sin t$$
$$+65(\sin^2\theta-\tfrac{2}{3})\cos(t-\phi)+5\sin^2\theta\cos(t+\phi).$$

This gives in units of $0{\cdot}1\,\gamma$ the following values for the north and west components :—

$$\mathrm{N} = (150\cos 2\theta-50\cos\theta+70\sin^2\theta\cos\phi)\cos t$$
$$+(-70\cos 2\theta-10\cos\theta+60\sin^2\theta\sin\phi)\sin t,$$

$$\mathrm{W} = (-70\cos\theta-10-10\sin\theta\sin\phi)\cos t$$
$$+(-150\cos\theta+50-10\sin\theta\cos\phi)\sin t.$$

The numerical values computed are shown in Table III.

Although the observed values are given in units of $0{\cdot}1\,\gamma$, it must be remembered that the accuracy in most cases does not exceed $1\,\gamma$.

I think it will be admitted that we have, on the whole, got a substantial representation of the data. The better agreement that might have been obtained for the European stations had, of course, to be sacrificed somewhat to get the curious features exhibited by the Bombay and Batavia data.

Table III.

Station.	N.		W.		V. (Provisional.)	
	a_1.	b_1.	a_1.	b_1.	a_1.	b_1.
Pavlovsk	+ 83	−16	−73	−84	+18	−50
Eskdalemuir	+ 77	−86	−67	−79	+20	−85
Wilhelmshaven	+ 70	−21	−67	−76	+24	−42
Potsdam	+ 64	−13	−67	−75	+26	−45
De Bilt	+ 65	−20	−66	−74	+25	−42
Pola	+ 32	+ 7	−61	−68	+82	−45
Helwan	− 49	+57	−49	−82	+29	−88
Bombay	−142	+87	−42	− 2	+ 4	−21
Batavia	−137	+59	−12	+69	−74	+13

The potential function obtained must also account for the values of V. We are at liberty to suppose that any term in Ω arises from an external or interior source, and further that these contributions may differ in phase. We may, therefore, introduce a division of the constants that will give the correct value of Ω at the surface and at the same time account for the observed values of V. In fact, if we could depend on the values of V we have the important means of determining the external and internal proportions. But unfortunately the observations of V are poor and everyone who has really faced the experimental difficulties admits that the results are most unsatisfactory. In particular I know that the Eskdalemuir results for V are quite unreliable, and, judging from the other data, I think they must be regarded with some suspicion. The Potsdam and De Bilt results do, however, agree very well, and so I take them as a sort of standard.

But clearly the position is a weak one, and therefore I do not feel justified in giving more than a general indication of what our formula would do.

I therefore assume that the outside and inside contributions agree in phase, and as regards the second order spherical harmonics I adopt Schuster's result that the internal contribution is one quarter of the external. In the first order harmonic I assume that the contribution from internal source is nil.

We thus get the formula for V.

$$V = \{150\sin\theta\cos\theta - 50\sin\theta + (70\ \sin^2\theta - 130/3)\cos\phi\}\cos t$$
$$+\{-70\sin\theta\cos\theta - 10\sin\theta + (60\ \sin^2\theta - 130/3)\sin\phi\}\sin t.$$

The computed values, marked provisional, are entered in Table III. The results are, on the whole, in the right direction, and might be brought closer by taking a smaller proportion from an internal source, but I do not think it worth while to force the matter until better data are available.

We now consider the 12-hour terms. The form which I found it convenient to try was

$$\Omega = \text{A} \sin^2\theta \cos\theta \cos(2t+\alpha_1) + \text{B} \sin^2\theta \cos(2t+\alpha_2)$$
$$+ \tfrac{1}{2}\text{C} \sin^3\theta \sin(2t+\phi-\phi') + \text{D} \sin\theta\,(\tfrac{4}{5}-\sin^2\theta) \sin(2t-\phi+\phi')$$
$$+ \text{E} \sin\theta \sin(2t-\phi+\phi').$$

The first four terms involve harmonics of order 3 but the last is of order 1.

I finally dropped the term in B, made $\text{E} = -\tfrac{4}{5}\text{D}$ and $\text{D} = \tfrac{1}{3}\text{C}$. It also seemed an advantage to make $\phi' = 30°$.

Thus the empirical form adopted was

$$10^6\,\Omega/a = \{-60 \sin^2\theta \cos\theta + 40 \sin^3\theta \sin(\phi-30°)\} \cos 2t$$
$$+ 25 \sin^2\theta \cos\theta \sin 2t,$$

so that $\text{C} = 60, \quad \text{D} = 20, \quad \text{E} = -16.$

The components to north and west thus become

$$\text{N} = \{-60 \sin\theta\,(2-3\sin^2\theta) + 120 \sin^2\theta \cos\theta \sin(\phi-30°)\} \cos 2t$$
$$+ 25 \sin\theta\,(2-3\sin^2\theta) \sin 2t,$$

$$\text{W} = \{60 \sin 2\theta - 80 \sin^2\theta \sin(\phi-30°)\} \sin 2t$$
$$+ \{25 \sin 2\theta + 40 \sin^2\theta \cos(\phi-30°)\} \cos 2t.$$

The computed values are shown in the following Table IV:—

Table IV.

Station.	N.		W.		V. (Provisional.)	
	a_2.	b_2.	a_2.	b_2.	a_2.	b_2.
Pavlovsk	−37	+16	+32	+52	−34	+ 8
Eskdalemuir	−50	+15	+35	+69	−44	+11
Wilhelmshaven	−47	+14	+37	+68	−45	+ 9
Potsdam	−43	+13	+39	+67	−47	+10
De Bilt	−47	+18	+38	+71	−49	+ 9
Pola	−32	+ 9	+44	+71	−58	+10
Helwan	+12	− 6	+52	+51	−59	+14
Bombay	+63	−16	+42	−12	−10	+24
Batavia	+45	−24	+ 8	−89	+69	+29

Again, I think these numbers give substantial agreement with the data.

Turning to the data for V, the numbers look more hopeful than in the case of the 24-hour terms, and the experimental errors that affect the 24-hour term are perhaps not so serious in the 12-hour term. Thus I was tempted to push the agreement somewhat further.

The data suggested that the main part for the northern stations arose from the term in $\sin^2\theta\cos\theta$, but was chiefly in the cosine term $\cos 2t$ and practically nil for the sine term $\sin 2t$. This can be met by assuming a phase difference between the outside and inside contributions. Thus I assumed

$$10^6\,\Omega/a = \mathrm{A}\frac{r^3}{a^3}\sin^2\theta\cos\theta\cos(2t-\epsilon_1)+\mathrm{B}\frac{a^4}{r^4}\sin^2\theta\cos\theta\cos(2t-\epsilon_2).$$

Hence we have

$$\mathrm{A}\cos\epsilon_1+\mathrm{B}\cos\epsilon_1 = -60, \qquad \mathrm{A}\sin\epsilon_1+\mathrm{B}\sin\epsilon_2 = 25.$$

To get the V results for Potsdam, we have the additional equations

$$3\mathrm{A}\cos\epsilon_1-4\mathrm{B}\cos\epsilon_2 = -120, \qquad 3\mathrm{A}\sin\epsilon_1-4\mathrm{B}\sin\epsilon_2 = 0.$$

Hence $\mathrm{A} = -53$, $\mathrm{B} = -14$, $\epsilon_1 = -15°$, $\epsilon_2 = -50°$, which agrees with Schuster's result that B is about 1/4 of A.

Next the term in $\sin^3\theta$ suggested the main part of the terms at Batavia, and assuming for the moment that the harmonic was entirely of order 3, I took the form

$$10^6\,\Omega/a = \sin^3\theta\sin(\phi-30)\left\{\mathrm{A}\frac{r^3}{a^4}\cos(2t-\epsilon_1)+\mathrm{B}\frac{a^4}{r^4}\cos(2t-\epsilon_2)\right\}.$$

Hence $\qquad \mathrm{A}\cos\epsilon_1+\mathrm{B}\cos\epsilon_2 = 40, \qquad \mathrm{A}\sin\epsilon_1+\mathrm{B}\sin\epsilon_2 = 0.$

The values at Batavia suggest taking

$$3\mathrm{A}\cos\epsilon_1-4\mathrm{B}\cos\epsilon_2 = 80, \qquad 3\mathrm{A}\sin\epsilon_1-4\mathrm{B}\sin\epsilon_2 = 40.$$

Hence $\qquad \mathrm{A} \doteq 35, \qquad \mathrm{B} = 8, \qquad \epsilon_1 = 9°, \qquad \epsilon_2 = -45°.$

This again makes B about one-fourth of A.

But the harmonic was really made up of a main part of order 3 and a minor part of order 1, and the correction to V is thus found to be

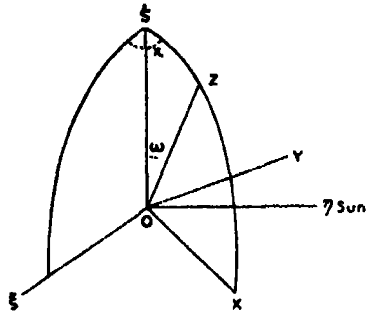
$$\sin\theta\,\{-16\sec 45°\sin(\phi+15°)\cos 2t+16\sec 45°\cos(\phi+15°)\sin 2t\},$$

where we have assumed that the first order term was entirely external. The net result is

$$\begin{aligned}\mathrm{V} = {} & \{-120\sin^2\theta\cos\theta+80\sin^3\theta\sin(\phi-30°)-23\sin\theta\sin(\phi+15°)\}\cos 2t \\ & +\{40\sin^3\theta\sin(\phi-30°)+23\sin\theta\cos(\phi+15°)\}\sin 2t.\end{aligned}$$

The computed values in Table IV seem to give very satisfactory agreement with the data

I do not, of course, suggest that this empirical representation of the data in Table I is unique or final, but I do think it is clear that the Schuster terms alone will not co-ordinate the data, and the form we have obtained does go a very considerable way towards meeting the difficulties.



We may now consider how the terms were arrived at, in such a way as to provide a clue to the physical meaning without binding oneself to any special theory.

In the figure let $O\xi$, $O\eta$, $O\zeta$, be rectangular axes through the earth's centre O, in the directions, earth's way, radius to the sun, and perpendicular to the plane of the ecliptic. Let OX, OY, OZ, be fixed rectangular axes in the earth, but not rotating with it, OZ being the axis of rotation, and OX in the plane containing $O\zeta$ and OZ. ω is thus the obliquity of the ecliptic and χ an angle expressing the time of the year.

The direction cosines of OX, OY, OZ, referred to $O\xi$, $O\eta$, $O\zeta$, are

$$\begin{array}{llll} \mathrm{OX} = & \cos\omega\cos\chi, & \cos\omega\sin\chi, & -\sin\omega\,; \\ \mathrm{OY} = & -\sin\chi, & \cos\chi, & 0\,; \\ \mathrm{OZ} = & \sin\omega\cos\chi, & \sin\omega\sin\chi, & \cos\omega. \end{array}$$

Let θ', ϕ' be the polar co-ordinates of a point fixed on the earth, and let θ, ϕ refer to any other point on the earth.

Suppose we start with a potential $\Omega = 1/r$ and differentiate along the direction θ', ϕ'. We get a new potential function

$$\Omega_1 = \left(\sin\theta'\cos\phi'\frac{\partial}{\partial x}+\sin\theta'\sin\phi'\frac{\partial}{\partial y}+\cos\theta'\frac{\partial}{\partial z}\right)\frac{1}{r}$$

$$= -\frac{1}{r^2}\{\sin\theta'\sin\theta\cos(\phi-\phi')+\cos\theta'\cos\theta\}.$$

Since $\phi-\phi'$ remains constant while the earth rotates, we simply have a contribution to the permanent field of the earth, representing a doublet with its axis in the direction θ', ϕ'. Again, let us differentiate along $O\eta$. We get

$$\Omega_2 = \frac{\partial}{\partial\eta}\frac{1}{r} = -\frac{\eta}{r^3}$$

$$= -\frac{1}{r^2}\{\sin\theta\cos\phi\cos\omega\sin\chi+\sin\theta\sin\phi\cos\chi+\cos\theta\sin\omega\sin\chi\}$$

$$= -\frac{1}{r^2}\{-(1-\sin^2\omega\sin^2\chi)^{\frac{1}{2}}\sin\theta\cos t+\cos\theta\sin\omega\sin\chi\},$$

where t is the local time at the point of observation reckoned from midnight.

The term in $\cos\theta$ contributes nothing to diurnal variation, but contributes a seasonal term to the general field. It has a maximum in summer, a minimum in winter, and vanishes at the equinoxes.

The term in $\sin\theta$ contributes to the diurnal variation. The amplitude has a semi-annual seasonal variation, rising to its maximum value 1 at the equinoxes, and falling to its minimum value $\cos\omega$ at the solstices.

Averaged for the year it contributes a term $\sin\theta\cos t$ to the mean diurnal variation.

Such a term is indicated by the data. We may, if we like, picture it as a uniform field in the direction of the sun, within which the earth rotates.

In a similar way we may differentiate along $O\xi$, and so get a term $\sin\theta\sin t$.

Let us now carry the process of forming functions further by differentiating Ω_1 along the direction $O\eta$. We may write the result in the form

$$\begin{aligned}\Omega_2 = \frac{1}{r^3}\{&3\sin\theta'\sin\omega\sin\chi\sin\theta\cos\theta\cos(\phi-\phi')-\cos\theta'\sin\omega\sin\chi(1-3\cos^2\theta)\\ &-3\cos\theta'\sin\theta\cos\theta(1-\sin^2\omega\sin^2\chi)^{\frac{1}{2}}\cos(\phi+t')\\ &-3\sin\theta'\sin^2\theta(1-\sin^2\omega\sin^2\chi)^{\frac{1}{2}}\cos(\phi+t')\cos(\phi-\phi')\\ &+\sin\theta'(1-\sin^2\omega\sin^2\chi)^{\frac{1}{2}}\cos(\phi'+t')\},\end{aligned}$$

where t' is Greenwich mean time, θ', ϕ' the co-ordinates of a point fixed with respect to Greenwich, and θ, ϕ the co-ordinates of the station referred to Greenwich.

The first two terms contribute nothing to diurnal variation, but only annual seasonal terms to the general field. The remaining terms contribute to diurnal variation, the amplitude having a semi-annual seasonal variation fluctuating between 1 and $\cos\omega$. Averaged for the year we get terms in the mean diurnal variation.

If θ' is 0 we have a term $\sin\theta\cos\theta\cos t$, where t is the local time. Similarly, a term $\sin\theta\cos\theta\sin t$ arises by differentiating along $O\xi$. We thus get the Schuster terms in the 24-hour term of diurnal variation.

If $\theta' = \frac{1}{2}\pi$, we have the term

$$3\sin^2\theta\cos(\phi+t')\cos(\phi-\phi')-\cos(\phi'+t'). \qquad \text{(A)}$$

Similarly, differentiating along $O\xi$, we get a term

$$3\sin^2\theta\sin(\phi+t')\cos(\phi-\phi')-\sin(\phi'+t').$$

Now, in this latter form replace ϕ' by $\frac{1}{2}\pi+\phi'$, as we are at liberty to do. We get

$$3\sin^2\theta\sin(\phi+t'),\sin(\phi-\phi')-\cos(\phi'+t'). \qquad \text{(B)}$$

Adding (A) and (B), we get

$$(3\sin^2\theta-2)\cos(\phi'+t'),$$

where t' is Greenwich mean time.

Again, deduct (B) from (A) and we get

$$3 \sin^2\theta \cos(2\phi - \phi' + t').$$

These are the terms we found it desirable to introduce.

We have thus obtained the terms required for the data, and clearly we might have taken a more general form had it been necessary.

We have seen that Schuster proposed to explain his term as arising from the permanent field and tidal oscillation. But there are great difficulties in the way. Our analysis confirms the association with the permanent field, but otherwise may simply mean differential conductivity of the air as between midday and midnight, and as between sunrise and sunset, the difference arising from the ultra-violet radiation from the sun.

As regards the term depending on Greenwich mean time, its mode of generation would appear to associate it with a magnetic axis lying in the plane of the equator. If there is such an axis the intensity will have to be feeble if it is not to produce a very pronounced influence on the general field, as indicated by observations.

My main objective has been the mean diurnal variation for the year, letting the seasonal variation take care of itself. But I anticipated that any correct method of approach would provide by extension for the seasonal change.

This appears to be the case in the analysis given. Seasonal change is provided for, but the terms we have obtained contribute only semi-annual change, not annual change.

The latter is important, but will not of course leave an influence on the mean yearly value. Thus it may be expected to arise in a way which differs from that we have already used. But differentiation along $O\zeta$ supplies the kind of function wanted.

Thus $$\frac{\partial\Omega}{\partial\zeta} = -\frac{1}{r^3}\{\cos\omega\cos\theta - \sin\omega\sin\theta\sin(t-\psi)\},$$

where t is the local time and $\tan\psi = \cos\omega\tan\chi$.

The first term contributes to the permanent field.

The second term contributes to the diurnal variation at any particular time of the year. But the phase ψ passes through a cycle in the course of the year, and so contributes nothing when averaged for a year.

The seasonal change is, however, beyond the limits I had prescribed myself in this paper, and I shall not pursue it further on this occasion.

So far the examination has referred to the 24-hour terms, but the data indicate the necessity for adding to the Schuster expression $\sin^2\theta\cos\theta\cos(2t+\alpha_2)$ in the 12-hour terms also. Our method for the

24-hour term suggests that we should get new 12-hour terms by a second differentiation along $O\xi$ or $O\eta$. The formulæ become more complicated if we are to retain the sun's annual variation in declination.

We therefore simplify the matter by regarding the sun as remaining in the plane of the equator. If we thus lose sight of the seasonal variation, we gain in conciseness.

If we take the form $\frac{\partial^2}{\partial\eta^2}\frac{1}{r}$, *i.e.* $\frac{\partial\Omega_2}{\partial\eta}$, we get as a potential form $-\frac{1-3\eta^2/r^2}{r^3}$ which leads to

$$-\frac{1}{r^3}\{(1-\tfrac{3}{2}\sin^2\theta)-\tfrac{3}{2}\sin^2\theta\cos 2t\}.$$

The contribution to the 12-hour term is of the form $\sin^2\theta\cos 2t$, but I did not find this term of much assistance in representing the data.

The Schuster term $\sin^2\theta\cos\theta$ arises by putting $\theta' = 0$ in Ω_1, which then becomes $\cos\theta/r^2$, and then forming the $\partial^2/\partial\eta^2$, $\partial^2/\partial\xi^2$, or $\partial^2/\partial\xi\partial\eta$ of $\cos\theta/r^2$.

If, on the other hand, we put $\theta' = \frac{1}{2}\pi$ in Ω_1, which then becomes $1/r^2 \,.\, \sin\theta\cos(\phi-\phi')$, and then form the $\partial^2/\partial\eta^2$, $\partial^2/\partial\xi^2$, or $\partial^2/\partial\xi\partial\eta$ of this, we arrive at 12-hour terms of the forms—

$$3\sin\theta\cos(\phi+\phi'+2t')-\tfrac{15}{2}\sin^3\theta\cos 2t\cos(\phi-\phi') \qquad \text{(C)}$$

and $$3\sin\theta\sin(\phi+\phi'+2t')-\tfrac{15}{2}\sin^3\theta\sin 2t\cos(\phi-\phi').$$

In the latter replace ϕ' by $\frac{1}{2}\pi+\phi'$. We get

$$3\sin\theta\cos(\phi+\phi'+2t)-\tfrac{15}{2}\sin^3\theta\sin 2t\sin(\phi-\phi'). \qquad \text{(D)}$$

Addition of (C) and (D) gives the form

$$\sin\theta\,(\tfrac{4}{5}-\sin^2\theta)\cos(2t+\phi'-\phi),$$

while, if we subtract (D) from (C), we get the form

$$\sin^3\theta\cos(2t+\phi-\phi').$$

I found it convenient to add to these forms a term $\sin\theta\cos(2t+\phi'-\phi)$ which may be regarded as a uniform field parallel to the plane of the equator rotating with the angular velocity of the earth but in the opposite direction.

We have thus formed a simple specification of the terms which seem to fit with the data. I have no theory to propose as to their origin, beyond Schuster's view that they arise from differential conductivity of the upper regions of the atmosphere. If further data confirm the probable reality of the terms, it should not be a difficult matter to express the law of conductivity which would account for them. As we have only had to proceed to second differentials with regard to the sun's direction, or the earth's way, it does not look as if the differential conductivity required is of a very complex nature.

The possibility of associating the electric and magnetic state of the earth with its translational movement has often attracted attention, although without success. It may not be out of place here to give a general solution of the electromagnetic equations for a body of conductivity c moving in a straight line with velocity kC, where C is the velocity of radiation. The solution, which I believe is new, refers to the steady state.

If (X, Y, Z) (α, β, γ) are the components of electric force and magnetic force the equations are

$$\left(-k\frac{\partial}{\partial x}+c\right)(\mathrm{X}, \mathrm{Y}, \mathrm{Z}) = \left(\frac{\partial\gamma}{\partial y}-\frac{\partial\beta}{\partial z},\ \frac{\partial\alpha}{\partial z}-\frac{\partial\gamma}{\partial x},\ \frac{\partial\beta}{\partial x}-\frac{\partial\alpha}{\partial y}\right),$$

$$\left(-k\frac{\partial}{\partial x}\right)(\alpha, \beta, \gamma) = \left(\frac{\partial \mathrm{Y}}{\partial z}-\frac{\partial \mathrm{Z}}{\partial y},\ \frac{\partial \mathrm{Z}}{\partial x}-\frac{\partial \mathrm{X}}{\partial y},\ \frac{\partial \mathrm{X}}{\partial y}-\frac{\partial \mathrm{Y}}{\partial x}\right),$$

and

$$\frac{\partial\alpha}{\partial x}+\frac{\partial\beta}{\partial y}+\frac{\partial\gamma}{\partial z} = 0,$$

$$\left(-k\frac{\partial}{\partial x}+c\right)\left(\frac{\partial \mathrm{X}}{\partial x}+\frac{\partial \mathrm{Y}}{\partial y}+\frac{\partial \mathrm{Z}}{\partial z}\right) = 0.$$

A solution is expressed by

$$\alpha = -(1-k^2)\frac{\partial\psi_0}{\partial x}-kc\psi_0, \quad \beta = -\frac{\partial\psi_0}{\partial y}, \quad \gamma = -\frac{\partial\psi_0}{\partial z};$$

$$\mathrm{X} = 0, \quad \mathrm{Y} = -k\frac{\partial\psi_0}{\partial z}, \quad \mathrm{Z} = k\frac{\partial\psi_0}{\partial y},$$

where ψ_0 is a solution of

$$(1-k^2)\frac{\partial^2\psi_0}{\partial x^2}+kc\frac{\partial\psi_0}{\partial x}+\frac{\partial^2\psi_0}{\partial y^2}+\frac{\partial^2\psi_0}{\partial z^2} = 0.$$

Primary solution—

$$\psi_0 = \frac{1}{\rho}e^{-\frac{kc}{2(1-k^2)}x\pm\frac{kc}{2(1-k^2)^{1/2}}\rho},$$

where

$$\rho^2 = \frac{x^2}{1-k^2}+y^2+z^2,$$

and other solutions may be obtained by the usual process of differentiation.

A Suggestion as to the Origin of Black Body Radiation.

By George W. Walker, A.R.C.Sc., M.A., F.R.S., formerly Fellow of Trinity College, Cambridge.

(Received October 15,—Read November 13, 1913.)

The discussion on "Radiation" in Section A at the recent British Association meeting in Birmingham was one of profound interest. Some of the remarks made then suggested the investigation which I now describe.

Planck's formula* for the emission function E_λ is

$$C^2h\lambda^{-5}/(e^{Ch/k\lambda T}-1).$$

This formula represents the observations for short and long waves at various temperatures with considerable closeness; and, if it is the correct expression, it is held by some to prove that the classical equations of dynamics and electrodynamics are at fault. As I do not think the classical equations are in much danger if properly applied, I have endeavoured to trace the dynamical explanation of the experimental data. There must be many formulæ which will express the data as well as Planck's form. In searching for such an expression of dynamical form, I went back to the equations for the motion of a charged sphere which I established on dynamical principles.† A clue to a solution very soon appeared, and without further remark, at present, I will state the formula that was tried.

If the emission within a range $\delta\lambda$ is expressed by

$$\phi(\lambda, \theta)\, d\lambda,$$

it will be remembered that, in order to satisfy Stefan's and Wien's laws, the expression $\theta^{-5}\phi(\lambda, \theta)$ must be a function of the product $\lambda\theta$.

Accordingly, I selected the formula

$$\phi(\lambda, \theta) = k\theta^5 \frac{\lambda^4\theta^4}{\{(\lambda^2\theta^2-a^2)^2+b^2\lambda^2\theta^2\}^2}$$

as a function which satisfies the following conditions:—

(1) It gives Stefan's law that the total radiation varies as θ^4, since

$$\int_0^\infty \frac{x^4}{\{(x^2-a^2)^2+b^2x^2\}^2}\, dx = \tfrac{1}{4}\pi/b^3 \qquad (a \neq 0 \text{ and } b+).$$

(2) It gives Wien's law that the maximum radiation at any temperature occurs when $\lambda_m\theta$ = constant. In our formula

$$\lambda_m\theta = a.$$

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* 'Theorie d. Wärmestrahlung,' 1906, p. 157.

† 'Phil. Trans.,' 1910, p. 152.

(3) It gives the condition that the maximum radiation at any temperature for this wave-length λ_m varies as θ^5. In our formula

$$\phi_{\text{max.}} = k\theta^5/b^4.$$

(4) It gives Lord Rayleigh's formula for long waves

$$\phi = k\theta/\lambda^4.$$

These conditions are required by the experimental work of Kurlbaum, Wien, Paschen, Lummer and Pringsheim, and Rubens.

The remaining point is therefore whether the formula will fit with the results of Paschen or Lummer and Pringsheim for short wave-lengths.

I take Lummer and Pringsheim's* data as typical.

It soon appeared that one might take $b^2 = 4a^2$, and then ϕ takes the simpler form

$$\phi = k\theta^5\left(\frac{\lambda\theta}{\lambda^2\theta^2+a^2}\right)^4.$$

We have at once from the data $\lambda_m\theta = a = 2940$ where the units are λ_m in microns (10^{-4} cm.), and θ in centigrade degrees absolute.

In computing the ordinates for any specified value of θ, it is convenient to note that for any wave-length λ equal to $n\lambda_m$ or $(1/n)\ \lambda_m$, the function ϕ varies as $(n+n^{-1})^{-4}$. The following are the numerical values of the function $f(n) = 16\,(n+n^{-1})^{-4}$:—

n.	$f(n)$	n.	$f(n)$
1·0	1·0	2·0	0·4096
1·1	0·9820	2·5	0·2262
1·2	0·9260	3·0	0·1292
1·3	0·8728	4·0	0·04904
1·4	0·8007	5·0	0·02188
1·5	0·7260	6·0	0·01106
1·6	0·6528	7·0	0·00615
1·7	0·5836	8·0	0·00367
1·8	0·5197	9·0	0·00232
1·9	0·4617	10·0	0·00154

I take the experimental curve of Lummer and Pringsheim† at temperature 1450° absolute, for which λ_m is practically $2\,\mu$, and choosing the scale to give a maximum ordinate of 73 units as shown in their diagram, the curve from our formula was calculated, and is shown in fig. 1. It fits the whole experimental curve excellently.

We have thus obtained a formula which fits all the data as well as, if not better than, Planck's. It is empirical, and there may be many others. But in form it suggests what we may expect from a dynamical system with very heavy damping.

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* 'Verh. d. Deutsch. Phys. Gesell.,' 1899, p. 213.

† *Loc. cit.*, p. 217.

The equation $$(m+m')\ddot{\xi}-k\dddot{\xi} = \mathrm{X},$$
where $$m' = \tfrac{2}{3}e^2/a\mathrm{C}^2 \quad \text{and} \quad k = m'a/\mathrm{C},$$
for the motion of an electron, has been much used by Lorentz, to whom we owe it, and by Planck. But it is only an approximate equation, although for many purposes a very good one.

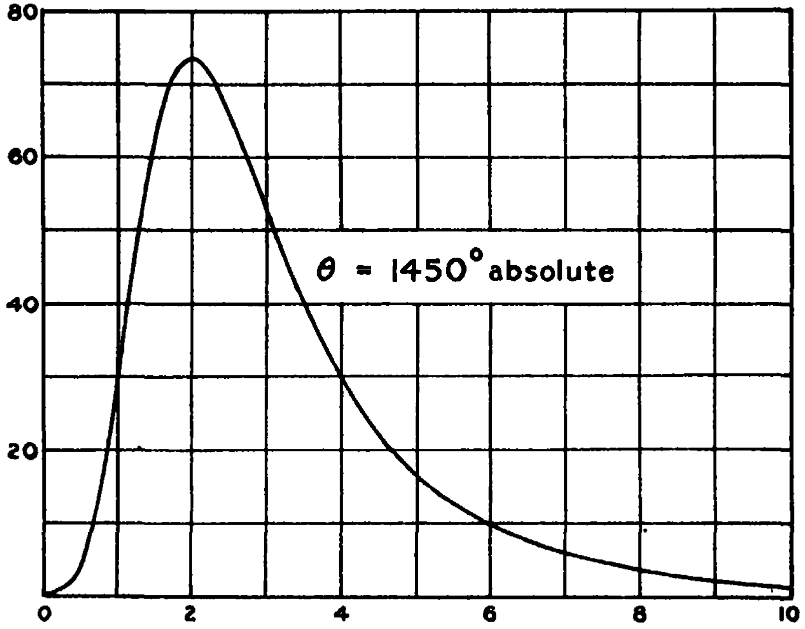

Fig. 1.

I have shown* that more correct expressions for the motion are given by the two equations

$$\frac{a^2}{\mathrm{C}^2}\ddot{\chi}+\frac{a}{\mathrm{C}}\dot{\chi}+\chi-e\frac{\dot{\xi}}{\mathrm{C}} = 0.$$

$$m\ddot{\xi}+\tfrac{2}{3}\frac{e}{a\mathrm{C}}\ddot{\chi} = \mathrm{X},$$

where χ is the value at $r = a$ of the function $\chi(\mathrm{C}t-r)$ which defines the state of the field in the æther, viz.,

$$(\mathrm{X}, \mathrm{Y}, \mathrm{Z}) = \frac{\mathrm{C}}{r^3}(-1, 0, 0)\left(r^2\chi''+r\chi'+\chi-e\frac{\dot{\xi}}{\mathrm{C}}\right)$$
$$+\frac{\mathrm{C}x}{r^5}(x, y, z)\left(r^2\chi''+3r\chi'+3\chi-3e\frac{\dot{\xi}}{\mathrm{C}}\right),$$

$$(\alpha, \beta, \gamma) = \frac{\mathrm{C}}{r^3}(0, -z, y)(r\chi''+\chi').$$

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* 'Phil. Trans.,' *loc. cit. ante.*

The equations were obtained first for a conductor, and were afterwards shown to be very nearly true for an insulating sphere.

Let us suppose that the restoring force is linear, so that $X = -\mu\xi$, and we then get

$$\frac{a^2}{C^2}\chi+\frac{a}{C}\dot{\chi}+\chi-e\frac{\xi}{C} = 0,$$

$$m\ddot{\xi}+\mu\xi+\tfrac{2}{3}\frac{e}{aC}\ddot{\chi} = 0.$$

Thus the free motion is determined by

$$\chi = Ae^{\lambda t}, \qquad \xi = Be^{\lambda t},$$

where
$$A\left(\frac{a^2}{C^2}\lambda^2+\frac{a}{C}\lambda+1\right) = B\frac{e}{C},$$

$$B\,(m\lambda^2+\mu)+\tfrac{2}{3}\frac{e}{aC}A\lambda^2 = 0.$$

Hence λ is a root of the equation

$$(m\lambda^2+\mu)\left(\frac{a^2}{C^2}\lambda^2+\frac{a}{C}\lambda+1\right)+m'\lambda^2 = 0.$$

If $m = 0$, we get

$$\left(m'+\mu\frac{a^2}{C^2}\right)\lambda^2+\mu\frac{a}{C}\lambda+\mu = 0,$$

of which the roots are, neglecting squares of a/C,

$$\lambda = \pm i\left(\frac{\mu}{m'}\right)^{\frac{1}{2}}-\tfrac{1}{2}\frac{\mu}{m'}\frac{a}{C}, \qquad \text{or} \qquad \lambda = \pm in-\tfrac{1}{2}n^2\frac{a}{C},$$

where n is the frequency.

This would agree with a calculation by Lorentz.

But experiments are against the supposition that m, the intrinsic mass of an electron, is zero, and Kaufmann's numbers suggest that m is of the same order as m'. For a positive particle it is generally agreed that m'/m is small.

Hence, retaining m, we get two pairs of complex roots. The approximate values neglecting squares of a/C are

$$\lambda = \pm in-\tfrac{1}{2}\frac{a}{C}\frac{m'}{m+m'}n^2,$$

where
$$n^2 = \frac{\mu}{m+m'} \quad \text{and} \quad \lambda = \pm\frac{i}{2}\frac{C}{a}\left(3+\frac{4m'}{m}\right)^{\frac{1}{2}}-\tfrac{1}{2}\frac{C}{a}.$$

These equations may be regarded as applicable to the behaviour of a molecule made up of a heavy, and so comparatively stationary, positive particle with a single electron revolving round it.

The vibrations are of two types. In the first, which closely agrees with

Lorentz' result, the damping is for optical purposes small, and the reduction of amplitude in the time between two collisions of a molecule with its neighbours would be small. But in the second type we have something very different.

The frequency is enormous and the damping so great for optical purposes that the reduction of amplitude to a small fraction of its original value may be regarded as instantaneous. Just after each encounter the amplitudes of the two types may be regarded as comparable, but before the next encounter the second type will have been suppressed by almost instantaneous radiation, while the first type will not have suffered any great reduction. Have we not here a clue to the "quantum" theory and the characteristic Röntgen radiation ?

In a detailed discussion it will be necessary to take account of the radiation from the positive particle also.

Let us now consider the steady radiation from an electron in which the motion is governed by the preceding equations and is maintained by a purely mechanical force $X_0 \cos pt$. The mean rate of radiation, viz., $\overline{X_0 \dot{x}}$, I find to be

$$= \frac{1}{3m^2}\frac{e^2}{C^3}p^4\frac{X_0^2}{D},$$

where
$$D = \left\{\left(p^2-\frac{\mu}{m}\right)\left(\frac{a^2p^2}{C^2}-1-\frac{m'}{m}\right)-\frac{m'}{m}\frac{\mu}{m}\right\}^2+\frac{p^2a^2}{C^4}\left(\frac{\mu}{m}-p^2\right)^2.$$

This result is equally applicable to a positive particle with appropriate values of m, m', and a. A similar result must hold when the joint action of a positive and negative combination is considered, and m, m' are a combination of the intrinsic and electric inertia terms, while a would now be a linear quantity defining the radius of the orbit.

The coefficient of X_0^2 is, as far as p or λ^{-1} enters, simply a generalised form of

$$\left(\frac{\lambda}{\lambda^2+\lambda_0^2}\right)^4,$$

and I have little doubt that it could be fitted with the data.

There are always three positive values of p^2 for which p^4/D is a maximum. These are in the vicinity of

$$p^2 = \frac{\mu}{m}, \quad p^2 = \frac{C}{a}\frac{\mu^{\frac{1}{2}}}{m^{\frac{1}{2}}}, \quad \text{and} \quad p^2 = \frac{C^2}{a^2}.$$

The corresponding maximum intensities are in the ratio $(m/m')^2$; 1 : 1 very nearly.

If we choose μ so that the first comes in the observed range of wave-lengths, the other two are in the ultra-violet, and if m'/m is small, they are of slight importance as compared with the first.

If, and only in so far as, Wien's and Stefan's laws are true, we require to suppose that a varies as θ^{-1} and μ varies as θ^2, and the expression is then a function of $\lambda\theta$. The reconciliation of these with each other and with the virial theorem of Clausius is a matter of difficulty, but as the experimental evidence is that neither law is strictly true, the matter may well rest for the present.

These considerations, and the present estimates of atomic magnitudes, lead me to suspect that black body radiation is determined not by the electron, nor by the positive particle alone, but by the joint action of the two. My conclusions are:—

(1) That the experimental data can be well represented by a formula of dynamical type, of which I have given one.

(2) That Newtonian dynamics and the electrodynamics of Larmor are capable of giving an explanation of that formula.

[*Note added October* 23, 1913.—Planck's radiation function has been applied by Einstein* and by Nernst† to the explanation of the variation of atomic heats with temperature. By similar reasoning I find that if the radiation function varies as

$$\theta^5\left(\frac{\lambda\theta}{\lambda^2\theta^2+a^2}\right)^4,$$

the typical term in the expression for the atomic heat varies as

$$\left(\frac{\theta^2}{\theta^2+\theta_0^2}\right)^4\left\{1+\frac{8\theta_0^2}{\theta^2+\theta_0^2}\right\},$$

where θ_0 is some definite temperature.

The following table gives the numerical values

θ/θ_0.	$f(\theta/\theta_0)$.	θ/θ_0.	$f(\theta/\theta_0)$.
0	0·000	4	1·153
1	0·312	5	1·112
2	1·065	10	1·037
3	1·181 maximum	∞	1·000

The result is similar to that required to explain the observations of Nernst.]

I would express my grateful thanks to Sir Joseph Larmor, who has discussed this paper with me, and by his suggestions has added so much to the manner of presenting the results.

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* 'Ann. d. Phys.,' 1907, vol. 22, p. 184.

† 'Sitzber. d. Berl. Akad.,' 1911, p. 494.

The Mathematical Representation of a Light Pulse.

By R. A. HOUSTOUN, M.A., Ph.D., D.Sc., Lecturer on Physical Optics in the University of Glasgow.

(Communicated by Prof. A. Gray, F.R.S. Received October 22,—Read November 27, 1913.)

In recent years, owing to the work of Rayleigh, Schuster, and others, our views as to the nature of white light have undergone a change, and it is now universally accepted that white light consists of irregular pulses which are transformed into trains of sine waves by their passage through a prism. But the method of this transformation is not clearly understood, as the reasoning on the subject is unfortunately somewhat general, the only concrete case well known being the pulse Rayleigh represented by $e^{-c^2t^2}$. Had the nature of a light pulse been better understood, there might possibly never have been any talk of the "Light Quantum" or unit theory of light.

The object of this note is to call attention to a new class of expressions representing the initial form and dispersion of a light pulse. They are both simple and elegant, and one of them gives the energy distribution required by Wien's law for black body radiation. They have been suggested by one of Kelvin's hydrodynamical papers.* They do not depend on the Fourier analysis and this is an advantage, for we never know how much of the latter is subjective.

Consider the equation

$$\frac{\partial^2 X}{\partial x^2} + c^2 \frac{\partial^4 X}{\partial t^4} = 0. \tag{1}$$

If we substitute $X = \sin \frac{2\pi}{\tau}\left(t - \frac{x}{v}\right)$, we find that $v = \pm \tau/2\pi c$, *i.e.* the equation represents the propagation of waves in a medium in which the velocity is directly proportional to the period. This is the law of deep-sea waves; it is obeyed by no medium for light waves although it gives the variation with the period in the right direction. After the necessary corrections have been made the distribution of the energy in the spectrum of an incandescent solid is independent of the prism producing the spectrum. Results obtained therefore for a hypothetical medium obeying the above law can easily be transferred to any other medium.

Equation (1) can be written

$$\frac{\partial X}{\partial (ix)} = \pm c \frac{\partial^2 X}{\partial t^2}.$$

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* "Initiation of Deep-Sea Waves, etc.," 'Proc. Roy. Soc. Edin.,' 1906, vol. 26, p. 399.

This is formally the same as the equation for the one-dimensional conduction of heat, namely,

$$\frac{\partial v}{\partial t} = \kappa \frac{\partial^2 v}{\partial x^2}.$$

Kelvin's instantaneous-plane-source solution for the latter is

$$\frac{1}{\sqrt{t}} e^{-x^2/4\kappa t}.$$

By analogy,
$$\frac{1}{\sqrt{(ix)}} e^{\mp t^2/4c(ix)},$$

is a solution of (1). Disregard the plus sign in the index and add a constant h to ix. The expression still satisfies (1) and becomes

$$\frac{1}{\sqrt{(h+ix)}} e^{-t^2/4c(h+ix)}. \qquad (2)$$

Since (1) is linear in X, we can differentiate (2) n times with regard to ix and the result,

$$\frac{\partial^n}{\partial (ix)^n} \frac{1}{\sqrt{(h+ix)}} e^{-t^2/4c(h+ix)}, \qquad (3)$$

is still a solution.

To find the initial form of this solution put $t = 0$ in (3) and then differentiate n times with respect to ix. The result is

$$(-1)^n \tfrac{1}{2} \tfrac{3}{2} \tfrac{5}{2} \ldots (n-\tfrac{1}{2}) \frac{1}{(h+ix)^{n+\frac{1}{2}}}.$$

Write $h+ix = \rho e^{i\theta}$, disregard the constant factor, and this becomes

$$\frac{\{\cos (n+\frac{1}{2})\theta - i \sin (n+\frac{1}{2})\theta\}}{\rho^{n+\frac{1}{2}}}.$$

We take the first part of this expression as the initial form, *i.e.* we choose the real part of (3). In fig. (1) the initial form of the disturbance is represented on the same scale for $n = 1, 2, 3, 4$, and 5.

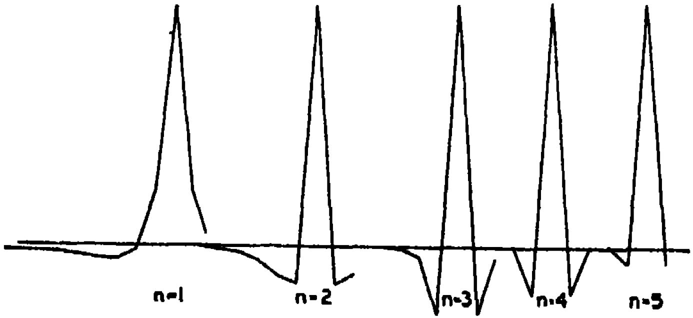

Fig. 1.

Kelvin has already (*loc. cit.*) treated the case of a deep-sea wave having the first of the above initial forms, and has shown how the disturbance spreads within a distance of a few wave-lengths from the origin. But it is here necessary to proceed quite otherwise, since in optics the observer is always at a much greater distance than this from the light source.

The quantity c is a constant for the medium. Let us fix it by supposing that a harmonic wave of wave-length $\lambda = 5 \times 10^{-5}$ cm. travels in the medium with a velocity of 3×10^{10} cm./sec. It has already been shown that the velocity of such a wave is $\tau/2\pi c$. Hence putting $\tau = 5 \times 10^{-5}/3 \times 10^{10}$ we obtain

$$3 \times 10^{10} = \frac{5 \times 10^{-5}}{2\pi c\,(3 \times 10^{10})},$$

or $$c = \frac{5 \times 10^{-5}}{2\pi\,(3 \times 10^{10})^2} = 9 \times 10^{-27} \text{ approximately, in (sec.}^2\text{/cm.).}$$

The initial disturbance is given by

$$\frac{\cos\,(n+\tfrac{1}{2})\,\theta}{\rho^{n+\frac{1}{2}}},$$

hence its value at the origin is $1/h^{n+\frac{1}{2}}$. If a be the abscissa of the point for which it has half its maximum value,

$$\frac{\cos\,(n+\tfrac{1}{2})\,\theta}{(h^2+a^2)^{(2n+1)/4}} = \frac{1}{2h^{n+\frac{1}{2}}},$$

$$(h^2+a^2)^{(2n+1)/4} < 2h^{n+\frac{1}{2}},$$

$$h^2+a^2 < h^2 2^{4/(2n+1)},$$

$$a^2 < h^2\,(2^{4/(2n+1)}-1),$$

a can be taken as a measure of the breadth of the initial disturbance.

We shall examine the disturbance when its maximum has travelled out a distance of 2 cm. from the origin, and shall suppose a small in comparison with 2 cm. Then in general h is small compared with 2 cm. A wave for which $\lambda = 5 \times 10^{-5}$ would take $\tfrac{2}{3} \times 10^{-10}$ secs. to travel out 2 cm., and an irregular disturbance will take something of the same order. While the disturbance is passing a point 2 cm. out, t will be about $\tfrac{2}{3} \times 10^{-10}$ secs., and consequently t^2/c approximately

$$\frac{(\tfrac{2}{3} \times 10^{-10})^2}{9 \times 10^{-27}} = 5 \times 10^5, \text{ in cms.}$$

The fact that t^2/c is so large simplifies things very considerably. In (3) the only term to be retained is that of the highest power in t^2/c, which is easily seen to be

$$\frac{1}{\sqrt{(h+ix)}}\left\{\frac{t^2}{4c\,(h+ix)^2}\right\}^n e^{-t^2/4c(h+ix)} = \frac{t^{2n}}{4^n c^n \rho^{2n+\frac{1}{2}} e^{i(2n+\frac{1}{2})\theta}}\, e^{-t^2 e^{-i\theta}/4c\rho}$$

$$= \frac{t^{2n}}{4^n c^n \rho^{2n+\frac{1}{2}}}\, e^{-t^2\cos\theta/4c\rho + i[t^2\sin\theta/4c\rho - (2n+\frac{1}{2})\theta]}.$$

Since h is small compared with x, we may write x for ρ, h/x for $\cos\theta$, and 1 for $\sin\theta$. Hence, making this substitution, taking the real part and omitting the $4^n c^n$ in the denominator, we obtain

$$\frac{t^{2n}}{x^{2n+\frac{1}{2}}}e^{-t^2h/4cx^2}\cos\left\{t^2/4cx-(2n+\tfrac{1}{2})\theta\right\},$$

where $\theta=\tan^{-1}x/h=\frac{1}{2}\pi$. Since $t^2/4c$ is of the order of $1{\cdot}25\times10^6$, the first term in the argument of the cosine varies very much more rapidly than the second. Disregard the second, therefore, and we obtain finally

$$\frac{t^{2n}}{x^{2n+\frac{1}{2}}}e^{-t^2h/4cx^2}\cos(t^2/4cx) \quad \text{or} \quad \mathrm{A}\cos(t^2/4cx). \tag{4}$$

We shall now find the manner in which the energy is distributed over the different wave-lengths for a given value of t. The wave-length at x is given by

$$\frac{t^2}{4c}\left(\frac{1}{x}-\frac{1}{x+\lambda}\right)=2\pi;$$

i.e.

$$\frac{t^2\lambda}{4cx^2}=2\pi \quad \text{or} \quad \lambda=\frac{8\pi cx^2}{t^2}.$$

It thus increases as the square of the distance from the origin. The energy in a distance dx is proportional to A^2dx. The change of wave-length in this distance is given by

$$d\lambda=d\left(\frac{8\pi cx^2}{t^2}\right)=\frac{16\pi cx\,dx}{t^2}.$$

The energy per wave-length is therefore

$$\mathrm{A}^2\frac{dx}{d\lambda}=\frac{t^{4n}}{x^{4n+1}}e^{-t^2h/2cx^2}\frac{t^2}{16\pi cx}=\left(\frac{t^2}{x^2}\right)^{2n+1}\frac{1}{16\pi c}e^{-(h/2c)(t^2/x^2)}.$$

Substitute $t^2/x^2=8\pi c/\lambda$; then the energy per wave-length is

$$\frac{(8\pi c)^{2n+1}}{\lambda^{2n+1}}\frac{1}{16\pi c}e^{-(h/2c)(8\pi c/\lambda)}=\frac{(8\pi c)^{2n}}{2}\frac{1}{\lambda^{2n+1}}e^{-4\pi h/\lambda}.$$

Wien's law for black body radiation is stated as

$$\frac{c_1}{\lambda^5}e^{-c_2/\lambda\mathrm{T}}.$$

If n is put $=2$, the two expressions agree. Hence the second of our initial pulses must be of exactly the same nature as that emitted by a black body. What is more, our symbol h varies inversely as T, the absolute temperature of the black body. The unexpected simplicity of the relation seems to promise well for the future of this way of regarding black body radiation.

As a check upon the analysis we can calculate the energy in the initial pulse. It is given in the general case by

$$\int_{-\infty}^{+\infty}\left(\frac{\cos\left(n+\frac{1}{2}\right)\theta}{\rho^{n+\frac{1}{2}}}\right)^2 dx.$$

Now, $x = h\tan\theta$; therefore, $dx = h\sec^2\theta\, d\theta$. Also, $\rho = h\sec\theta$. On substitution the integral becomes

$$\frac{2}{h^{2n}}\int_0^{\pi/2}\cos^2\left(n+\tfrac{1}{2}\right)\theta\cos\theta^{2n-1}\,d\theta.$$

If $n = 2$, this varies as the inverse fourth power of h or the direct fourth power of T. We have thus arrived at Stefan's law of black body radiation.

Let us now definitely make $n = 2$ and examine the shape of the pulse when its maximum has travelled 2 cm. from the origin. For the maximum

$$\frac{d}{dx}\frac{1}{x^{9/2}}e^{-t^2h/4cx^2} = 0,$$

which gives $t = x\surd(9c/h)$. We see incidentally that the group velocity is $\surd(h/9c)$. Write 2 for x in this expression for t and substitute the result in (4), at the same time putting $n = 2$. If we omit the constant factor, (4) then becomes

$$\frac{1}{x^{9/2}}e^{-9/x^2}\cos(9/hx).$$

This expression gives the disturbance as a function of x, and it is represented in fig. 2. To make the figure clear h has been given the very large value of $\frac{1}{15}$.

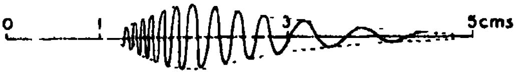

Fig. 2.

It will be seen from fig. 2 that the initial pulse has been dispersed by the medium into a train of waves all comprised between 1 and 5 cm., the long waves coming first and the wave-length gradually decreasing as we get to the rear of the train. There is, of course, a similar train travelling the other way at the same distance on the other side of the origin. The wave-length at the point of maximum amplitude, *i.e.* the dominant wave-length, is obtained by combining

$$\lambda = \frac{8\pi cx^2}{t^2} \quad \text{and} \quad t = x\surd(9c/h).$$

It is therefore $\frac{8}{9}\pi h$ and is always the same, *i.e.* the same wave-length always rides on the crest of the group. In the case represented in fig 2, the dominant wave-length is $8\pi/(9\times 15) = 0{\cdot}186$ cm., a very long heat wave. If it were green, at that distance out there should be roughly 3500 times as many wave-lengths in the train, but, of course, the number always increases the further the group goes.

The period of a wave τ is given by

$$\frac{1}{4cx}\left\{(t+\tau)^2-t^2\right\} = 2\pi,$$

i.e.
$$\frac{2t\tau}{4cx} = 2\pi \quad \text{or} \quad \tau = \frac{4\pi cx}{t}.$$

Hence the wave-velocity, v, is

$$\frac{\lambda}{\tau} = \frac{8\pi cx^2}{t^2}\,\frac{t}{4\pi cx} = \frac{2x}{t} = \frac{4\pi cx}{t}\,\frac{1}{2\pi c} = \frac{\tau}{2\pi c},$$

the same value as was obtained by substitution in equation (1).

The dispersive power of a medium is usually specified by

$$\frac{\mu_F-\mu_C}{\mu_D-1}.$$

In our hypothetical medium the velocity varies as the wave-length, and the velocity for $\lambda = 5\times 10^{-5}$ is 3×10^{10} cm./sec. Consequently μ_D is not far from 1, and it seems more reasonable to measure the dispersive power simply by $\mu_F-\mu_C$, which has the value

$$\frac{5000}{4851}-\frac{5000}{6563} = 0{\cdot}27.$$

For flint glass $\mu_F-\mu_C$ has the value $0{\cdot}0193$ and for air the value $3{\cdot}1\times 10^{-6}$; hence the dispersive power of our hypothetical medium is roughly 14 times that of flint glass and 10^5 times that of air.

I am indebted to Dr. George Green for suggesting that Kelvin's hydrodynamical solutions might be applied to optics; also for showing me an original derivation of Rayleigh's energy law by the application of group velocity.

Note on the Colour of Zircons, and its Radioactive Origin.

By the Hon. R. J. STRUTT, M.A., Sc.D., F.R.S., Professor of Physics, Imperial College, South Kensington.

(Received November 11,—Read November 27, 1913.)

Crystals of the mineral zircon are found in a variety of different colours. What I have to communicate refers to the brown kinds. Of these, two may be distinguished: the common opaque brown variety, easily obtained in large quantity from the South of Norway and from North Carolina, and the transparent reddish brown kinds known as hyacinth, and obtained, for instance, from Expailly in Auvergne, from Unkel, on the Rhine, and from Campbell Island, New Zealand. It is remarkable that the opaque kinds occur in plutonic rocks, such as syenites, and the transparent (when their matrix can be traced) only in basalts and other lavas. Their outline is rounded, even when found, as at Unkel, embedded in perfectly fresh basalt. For this reason it has been supposed (and I have no doubt correctly) that such zircons have been derived from the melting down of plutonic rocks which originally contained them. Zircon, from its extreme resistance to chemical attack, would survive almost all other minerals. Incipient chemical attack would account for the rounded shape, which is in extreme contrast to the sharp crystal outline of the zircons in their original home in plutonic rocks.

Hyacinths lose their reddish brown colour completely when heated to a temperature of about 300° C., and this fact, considered in relation to their occurrence embedded in a solidified lava, presents at first sight no small difficulty. How is it that they were not decolorised by the heat of the molten rock? Or, if they were decolorised, how has the colour been recovered? For it will hardly be suggested that transparent crystals of a material so resistant have been coloured by any action of percolating water

Another somewhat similar difficulty is raised by the fact that these transparent zircons are thermoluminescent. The crystals, when moderately heated, give out a phosphorescent glow, at the same time that they lose their colour. But this glow does not recur on a second heating of the specimen, and the question presses for answer, How has the capacity to glow been recovered?—for presumably it was not present in the crystals when they first cooled down in their matrix of molten lava.

It is known that the crystals decolorised by heat have their colour restored by exposure to radium. One day's exposure to a few milligrams of radium produces a distinct effect in restoring the colour.

Exposure to radium also restores the property of thermoluminescence.

Now, as I showed some years ago,[*] zircon is a distinctly radioactive mineral, containing hundred of times as much radioactive matter as ordinary rock masses. It is suggested, therefore, that *the zircons found in lavas have had their colour and thermoluminescence restored by the slow action, during prolonged ages, of the radium they themselves contain.*

On this view, it might appear that the depth of colour, taken with the amount of radioactive material present, and the observed rate of coloration by radium would give a means of estimating the time which had elapsed since the lava matrix became cool. Unfortunately, however, the colour of the zircons is *saturated*, that is to say, further exposure to radioactive matter does not deepen it. To test this point, two transparent brownish-red hyacinths from Expailly were ground down to slices about 0·75 mm. thick. These were examined under a low microscopic power, as their area was somewhat small for naked eye comparison, and the depth of tint which they each showed by transmitted light was found to be as nearly as possible the same. One slice was exposed on the surface of 5 mgrm. of radium bromide with a very thin layer of mica interposed. After the lapse of a month, the tint was scarcely, if at all, deeper than that of the other, which had been reserved for comparison. The specimen was then decolorised by heat and again exposed to the radium. In four days it had recovered the original tint and did not get any darker with further exposure.[†]

We cannot, therefore, determine from the depth of colour what time has elapsed since the specimen cooled. It should be possible to find an inferior limit to it, and this might be of interest in connection with the general question of geological time, for the hyacinths of Expailly (for instance) occur in basalt which is overlain by strata containing extinct mammalian remains.[‡]

The chief difficulty in finding such a limit is this: The α-rays are probably the chief agent concerned in the colouring process, and as these only penetrate distances of the order of $\frac{1}{50}$ mm., it would be necessary in determining experimentally the rate of coloration by strong radioactive preparations, to use slices of decolourised zircon of some such thickness as this. Unfortunately the colour producible in such thin layers is much too faint for measurement, and it would be necessary to superpose many of them. This would greatly complicate the experiment.

The opaque brown zircons mentioned at the beginning of this note seem to be in a different state from the transparent hyacinths. For, as originally found, they are not thermoluminescent, nor can they be made so by exposure to radium. Moreover they are not decolorised by moderate heating.

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[*] 'Roy. Soc. Proc.,' 1906, A, vol. 78, p. 152.

[†] Decolorising by heat and recolouring by radium can be repeated indefinitely.

[‡] See Scrope, 'Geology of Central France.'

As already explained, there is reason to believe that hyacinths are formed from these opaque zircons by the action of a bath of molten basalt. It was attempted, and with partial success, to imitate this experimentally. Basalt was kept melted in a platinum crucible over a gas furnace, and some opaque zircons immersed in it for 24 hours. After this they were extracted, and found to be quite white, though not transparent. On exposure to radium they now took on the redder colour of hyacinths and became, like them thermoluminescent.

The only outstanding point is the transparency of natural hyacinths. This may result in some way from the gently increasing, very prolonged action of the molten basalt under geological conditions, which cannot be artificially imitated.

Intermittent Vision.

By A. Mallock, F.R.S.

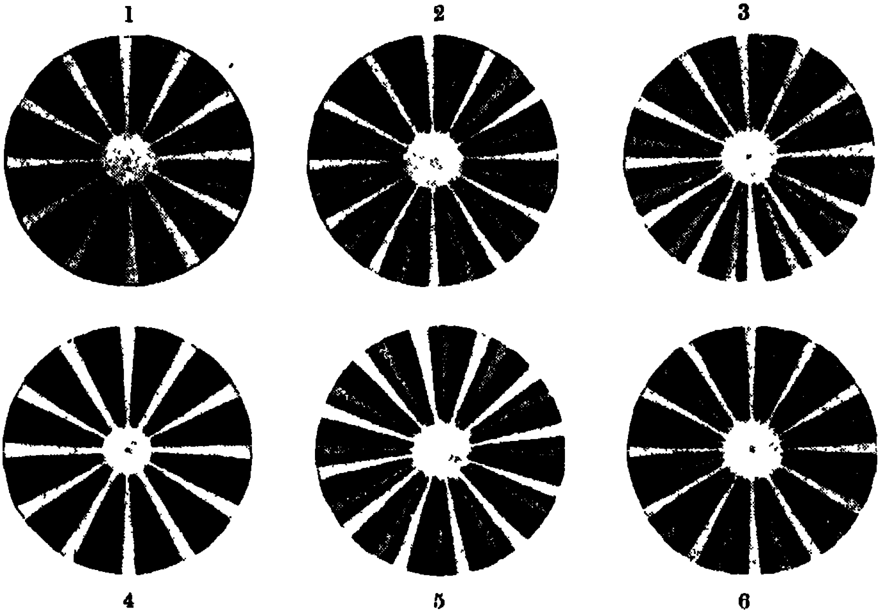
(Received November 11,—Read December 11, 1913.)

It is a matter of fairly common observation that the spokes of the wheels of passing motor cars often appear momentarily stationary, and sometimes even seem to be turning in the direction opposite to their actual motion. It was pointed out to me by the Hon. T. F. Fremantle that these appearances, which last only for a small fraction of a second, coincide with the steps of the observer, and are only noticeable when the speed of the vehicle lies between certain limits. On the one hand the motion must be too quick for the eye to follow the individual spokes, and on the other it must not exceed a certain limit, which is apparently slightly different for different individuals.

To examine the phenomena more closely and conveniently a 4-inch disc of black paper was prepared, on which 12 equally spaced radial white lines were superposed, and the disc was mounted on a heavy top, running on ball bearings, and which when spun lost its speed slowly. An electric contact on the top in conjunction with a recording chronograph gave the angular speed at each instant, while another pen worked by the observer allowed signals to be marked on the chronograph paper, indicating according to a code the nature of the appearance of the disc in various circumstances.

It was found that the lines on the spinning disc appeared stationary not only at each step, but that any slight mechanical shock, such as is given by gently tapping the head or body, or by working the jaws or by winking, was equally efficacious. When the speed was so low that only 9 or 10 lines passed a fixed point in a second, the appearance was merely that of ordinary "flicker" and when 80 or more lines passed in the same time the surface looked uniformly grey, and in both cases mechanical shock had no apparent effect.

Figs. 1–6 give an idea of the impression received at various speeds of rotation.



Figs. 1–6.

The first thing noticeable after the angular velocity drops to about six revolutions per second (*i.e.* about 70 lines per second) is that at each shock the uniform grey surface seems to break into a number of radial lines; it is difficult to estimate their number, but a guess would put it between 40 and 50. This is the conventional way in which rapid rotation is suggested in drawings. When the speed has dropped to about 4·5 revolutions per second, the lines appear equally spaced (*i.e.* at intervals of 15°), fig. 6. At three revolutions per second the appearance is that of fig. 4, the lines being separated by their natural intervals of 30°. Above and below this speed the lines again are grouped in pairs (figs. 3 and 5), and at 1·5 revolutions, the spacing becomes uniform at 15°, see fig. 2, rather better defined than in the corresponding fig. 6.

At a lower speed still the lines again appear in pairs (fig. 1), but now flickering tends to obscure the effect.

The intensity of the light has a good deal of influence on the result. In a feeble light very little can be seen of stationary images, and when the light is very strong flickering interferes before the stage shown in fig. 2 is reached.

An explanation of the above-mentioned phenomena can be given on the assumption that a slight mechanical shock of any kind produces a periodic but rapidly extinguished paralysis of the perception of light. (I have reason to believe that something of the same kind happens as regards sound but the observations in this case are not so easily made.)

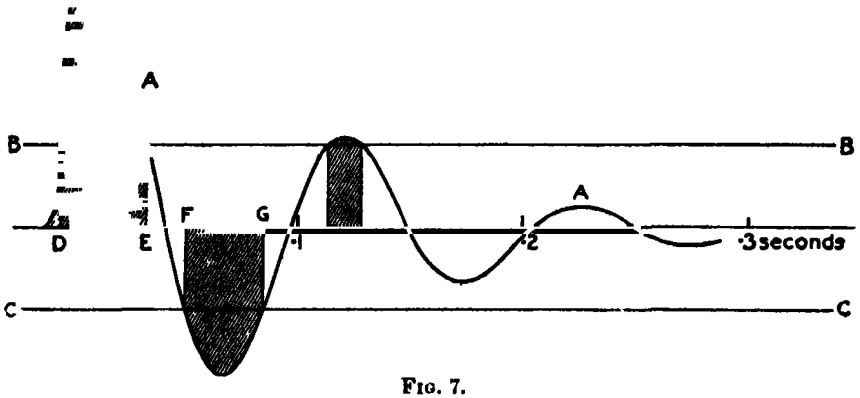


FIG. 7.

Suppose that the nerves on which "seeing" depends cannot bear more than a certain amount of mechanical acceleration without loss of sensibility, and let the curve A, fig. 7, represent the mechanical acceleration consequent on a shock or blow of any kind. Let B and C be two lines giving the limits of acceleration which does not produce loss of sensation.

Then the effect of the shock will be to extinguish the image of a bright object for the times indicated by the length of the shaded parts of diagram. The first recurrence of the image after the shock will last for a short time only, and thus if the object is in motion a fairly defined image of it will be seen at a distance from the first disappearance equal to its travel in the time DE.

As the vibration consequent on the shock dies out the time of visibility increases, the next eclipse being represented by FG, and so on.

For the class of shocks which are considered here only two or at most three secondary images can be made out.

More severe shocks cause a displacement of the directions of the eye which displaces the image on the retina, and it is difficult to say what is seen; but mechanical displacement of the image on the retina without loss of sensibility does not explain the observed facts. For, in this case, only those lines would be affected which were considerably inclined to the direction of vibration; and although the direction of the vibration (*e.g.* the application of the shock to the top or sides of the head) has some effect on the pattern of the stationary lines, the differences are not large, and any shock makes all the radial lines visible, though in a slightly different degree.

If the explanation suggested in this paper is correct it will be seen from fig. 7 that there are two intervals of eclipse to each complete vibration, and that since, when the disc makes three revolutions per second, the lines have turned through their natural interval of 30° before sensibility is restored, the period is 18 per second.

The chief interest of this intermittent vision lies in the definite period involved. What determines the period, however, is not clear; it may be merely the mechanical period of the head on its elastic supports, or on the other hand it may be a period belonging to the brain or nerves. That such a slight shock as that caused by opening the eyelids is effective, rather suggests the latter origin, whilst the fact that when the shock is caused by tapping the head or body the effect increases with the strength of the blow, is more consistent with a vibration of the head as a whole.

A Method of Measuring the Pressure Produced in the Detonation of High Explosives or by the Impact of Bullets.

By Bertram Hopkinson, F.R.S.

(Received October 17,—Read November 27, 1913.)

(Abstract.)

If a rifle bullet be fired against the end of a cylindrical steel rod, or some gun-cotton be detonated in its neighbourhood, a wave of pressure is transmitted along the rod with the velocity of sound. If the pressure in different sections of the rod be plotted at any instant of time, the abscissæ being distances along the rod, then at a later time the same curve shifted through a distance proportional to the time will represent the then distribution of pressure. Also the same curve represents the relation between the pressure across any section of the rod and the time, the scale of time being approximately 2 inches for 10^{-5} seconds. In particular it represents the relation between the total pressure applied to the end of the rod and the time, and the length of the curve represents the total duration of the blow.

If the rod be divided at a point a few inches from the far end, the opposed surfaces of the cut being in firm contact and carefully faced, the wave of pressure travels practically unchanged through the joint. At the free end it is reflected as a wave of tension, and the pressure at any section is then to be obtained by adding the effects of the pressure wave and the tension wave. At the joint the pressure continues to act until the head of the reflected tension wave arrives there. If the tail of the pressure wave has then passed the joint the end-piece flies off, having trapped within it the whole of the momentum of the blow, and the rest of the rod is left completely at rest. The length of end-piece which is just sufficient completely to stop the rod is half the length of the pressure wave, and the duration of the blow is twice the time taken by the pressure wave to travel the length of the end-piece. Further, it is easy to see, as is proved in detail in the paper, that the momentum trapped in quite short end-pieces will be equal to the maximum pressure multiplied by twice the time taken by the wave in traversing the end-piece. Thus by experimenting with different lengths of end-pieces and determining the momentum with which each flies off the rod as the result of the blow it is possible to measure both the duration of the blow and the maximum pressure developed by it. This is the basis of the experimental method described in the paper. A steel rod is hung up as a ballistic pendulum, and the piece is held on to the end by magnetic attraction.

A bullet is fired at the other end, and the end-piece is caught in a ballistic pendulum and its momentum measured. The momentum of the rod is also measured.

Most of the experiments described in the paper were made with lead bullets with the object of checking the accuracy of the method. On the assumption that a lead bullet behaves on impact as a fluid the time taken completely to stop it, which is the duration of the blow, is equal to the time which it takes to travel its own length, and the maximum pressure is equal to the mass per unit of length in the section of greatest area multiplied by the square of the velocity. The experiments showed good agreement between the observed and calculated values of the maximum pressure as is shown in the following table:—

Velocity of bullet.	Maximum pressure.	
	Calculated.	Observed.
ft./sec.	lb.	lb.
2000	43,500	42,600
1240	15,700	16,700
700	5,450	5,320

The observed duration of the blow is in the case of the highest velocity about 6 per cent. greater than the time taken by the bullet to travel its own length. This discrepancy is to be accounted for partly by the fact that the bullet is really not absolutely fluid, but is also in part due to the non-fulfilment of some of the conditions postulated in the simple theory of the method. It seems probable that the principal source of error of the latter kind is that the pressure applied by the bullet is not uniformly distributed over the end. Experiments with rods of different diameter show that the larger ones give larger estimates of the duration of the impact.

Having established by experiments on lead bullets that the method of experiment is capable of giving within a few per cent. both the maximum pressure and the duration of very violent blows, experiments were next made on the detonation of gun-cotton. Cylinders of dry gun-cotton 1¼ inch × 1¼ inch and weighing about 1 oz. were detonated with fulminate at a distance of about ¾ inch from the end of the steel rod. The results may be expressed by saying that the average value of the pressure during a period of 10^{-5} seconds in the neighbourhood of the maximum is about thirty tons per square inch. The absolute maximum is of course considerably higher. The pressure has practically disappeared in 1/50,000 second, that is at least 80 per cent. of the impulse of the blow has been delivered within that time. Experiments were also made with gun-cotton in contact with the rod, but owing to the permanent deformation of the steel, which would have the effect of deadening the blow, the results in this case cannot claim to be precise. They lead, however, to the conclusion that the maximum pressure at the surface of contact is at least double what it is when an air-space ¾ inch thick is interposed.

The results obtained for gun-cotton, though lacking in precision, throw some light on the nature of the fracture which is produced by the detonation of this explosive in contact with a mild steel plate. They show that the pressure of the gun-cotton may be regarded as an impulsive force in the sense that only very small displacement of the steel occurs during its action. Its effect is to give velocity to the parts of the plate with which it is in contact, the remainder being left at rest. In a plate 1 inch thick the velocity given by a slab of gun-cotton of about the same thickness is roughly 200 feet per second. The resulting strain depends upon the ratio of this velocity to the velocity of propagation of waves of stress into the material, and, assuming perfect elasticity, shearing stresses of the order of 100 tons per square inch may be produced in a plate of this thickness. In static tests on mild steel the metal flows when the shearing stress is of the order of 10 tons per square inch, and no materially greater stress can exist. But if the rate of straining is sufficient, the viscosity of the flowing metal becomes important, and the shearing stress may approximate to the value corresponding to perfect elasticity. The shearing stress is accompanied by tension, which under such circumstances may be sufficient to break down the forces of cohesion. Thus the steel is cracked in spite of its ductility, just as pitch may be cracked by the blow of a hammer. From the measured duration of the pressure produced by gun-cotton it may be inferred that the velocity of shear required to crack mild steel is of the order of 1000 radians per second.

The shattering of the plate by the gun-cotton probably occurs during the time that the pressure is acting—that is within two or three hundred-thousandths of a second—and before the plate has had time to be sensibly deformed. The bending of the broken pieces, which is always found when mild steel is broken in this way, occurs subsequently, and is due to the relative velocities which remain in the different parts of each piece of the plate after the plate has been broken and the pressure has ceased to act.

The Selective Absorption of Ketones.

By Prof. George Gerald Henderson, D.Sc., LL.D., and Isidor Morris Heilbron, Ph.D.

(Communicated by Dr. G. T. Beilby, F.R.S. Received October 23,—Read December 11, 1913.)

The absorption of light by carbon compounds is either continuous or selective, although not infrequently both kinds of absorption are found to occur together. In the visible and ultra-violet portions of the spectrum the absorption is decidedly a constitutive property of the compound; apparently the only additive relation is the effect of increasing the mass of the molecule, as, for instance, in homologous series, when displacement of the absorption band towards the red accompanies increase in the molecular weights.

Hartley's pioneer work on absorption led him to recognise clearly the dynamic nature of this property, and to arrive at the conclusion that it is caused by the vibrations of sub-molecular particles synchronising with those of the incident waves of light. Support is lent to this conclusion by the observation that the absorption and emission spectra of simple substances are identical. As regards the nature of the particles to whose vibrations selective absorption is due, Hartley originally expressed the view that these must be atoms, or groups of atoms. More recent investigations confirm this opinion so far as the infra-red region is concerned; but, on the other hand, according to Drude's work on the electronic theory of dispersion and absorption, the particles whose oscillations cause selective absorption in the visible and ultra-violet regions are sub-atomic and probably correspond to the valency electrons. If this be so, the relations between the absorption and the constitution of carbon compounds must be sought in the dynamic state of the valencies of the absorbing group of atoms.

As a general rule carbon compounds which exhibit selective absorption belong to the cyclic class, whilst aliphatic compounds show merely a weak general absorption. This rule, however, is not without exceptions, for it is now known that many aliphatic ketones, as well as their derivatives, which contain the $—CH_2—CO—$ or the $—CO—CO—$ group absorb selectively in the visible or the ultra-violet region. Some at least of these compounds are capable of existing in tautomeric modifications, namely a keto form $R.CH_2.CO.R'$ and an enol form $R.CH{:}C(OH).R'$, and it has been suggested that the absorption of these compounds is due to some intramolecular vibration which occurs when one tautomeric form changes into the other.

It is highly improbable that the oscillation of the labile hydrogen atom between the carbon and the oxygen atoms, $R.CH_2.CO.R' \rightleftarrows R.CH:C(OH).R'$, is the immediate cause of the vibration, because the oscillation frequency of the absorption band is not materially changed when that hydrogen atom is replaced by a metallic atom of very much greater mass. According to the electronic theory the linkage between the atoms of a compound is formed by the migration of an electron, or a group of electrons, from one atom to the other, and a change of linkage must be accompanied by a movement of these valency electrons. Hence it is concluded that the absorption of such ketones must be due to the electronic disturbance which results from the change of one tautomeric form to the other.

The authors have studied the absorption spectra of a number of compounds containing the $—CH_2—CO—$ or the $—CO—CO—$ group, as well as of such derivatives as their semicarbazones, and are unable, for several reasons, to accept the view that the electronic disturbances which, doubtless, are the primary cause of absorption are the result of any tautomeric change. Thus the aliphatic ketones of the type $R.CO.R'$ exhibit selective absorption, and yet it has been shown by a strictly chemical method that these compounds are entirely ketonic in structure, no trace of an enol form being perceptible even in presence of alkali. Again, ethyl acetoacetate exists in a keto form, $CH_3.CO.CH_2.CO_2Et$, and an enol form, $CH_3.C(OH):CH.CO_2Et$; neither form of itself exhibits selective absorption, but addition of alkali to each has the effect of producing a banded spectrum; yet it has been proved that the characteristic absorption band is entirely independent of tautomeric keto-enol oscillation. Again, the authors' results show that the oscillations which cause the selective absorption exhibited by the aliphatic ketones must be of the same type in each of these compounds, since each gives the same band, and consequently the suggested relationship between selective absorption and the activity of the carbonyl group in ketones induced by a keto-enol change cannot exist.

The view has been advanced that in ketones the intramolecular vibration takes place primarily within the carbonyl group, which is to be regarded as the oscillation centre of those compounds. We hold that this is a correct view, and that if the residual valency of the carbonyl group is taken into account it is possible to form a conception of a type of intramolecular oscillation which may be the cause of the selective absorption exhibited by ketones and their derivatives.

Gebhardt's theory of valency postulates for each atom a maximum affinity, which may or may not be fully called into play when atomic linkage takes place. Hence, since the total affinity of each atom remains constant, if for any reason the bond between linked atoms is weakened residual affinity must appear on each as a free partial or "ionised" valency. Such free partial valencies, which are capable of acting as subsidiary affinity forces, are most likely to appear on atoms linked by a double bond; for example, the atoms of the carbonyl group (>C=O); or else may first be called into existence by other influences.

Accepting these ideas in modified form, we suggest, firstly, that selective absorption in ketones is caused by intramolecular vibrations, due to the alternate formation and breaking down of unstable ring systems, and, secondly, that the momentary formation of those ring systems is effected through the agency of free partial valencies, which, under certain conditions, make their appearance on the atoms of the compound.

In order to illustrate this suggestion, the case of acetone, $CH_3.CO.CH_3$, may be considered. According to our view, it is possible for free partial valencies to appear on the carbon and the oxygen atom of the carbonyl group of this compound, because the bond between those atoms will be weakened by the attractive influence of a hydrogen atom on the oxygen atom. The momentary linkage, through a partial valency, of this hydrogen atom to the oxygen atom will weaken the bond between the former and the carbon atom to which it is linked, and a free partial valency will appear on this carbon atom also. Fig. 1, in which, as in the other figures, partial valencies are indicated by dotted lines, represents this phase—

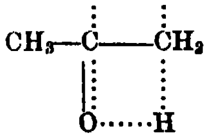


Fig. 1.

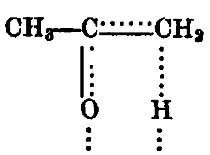


Fig. 2.

The free partial valencies on the carbon atoms will tend to unite, but, we suppose, can only do so by drawing upon the affinity of the oxygen and hydrogen atoms, with the result that the partial linkage between them will be broken down and the phase represented in fig. 2 will be formed. This phase also will only have a momentary existence, because whenever the free partial valencies on the carbon atoms have neutralised each other, the first phase will be reproduced. In short, there will be an intramolecular oscillation between the two phases, and it is to the electronic disturbances which accompany this oscillation that, we believe, the selective absorption of acetone is to be attributed.

According to this view precisely similar oscillations should take place within the molecules of the homologues of acetone, and therefore each of these ketones should exhibit essentially the same absorption curve as acetone. Our experiments prove that this is actually the case. Moreover, we have found that the semicarbazones of acetone and its homologues, *e.g.*, $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C{=}N.NH.CO.NH_2$, exhibit only general absorption, and this result also is indicated by our hypothesis, for although in these compounds there is a double linkage between a carbon and a nitrogen atom, yet the attraction between hydrogen and nitrogen is not sufficiently strong to cause the appearance of free partial valencies, hence the resulting intramolecular vibrations do not occur.

The idea of intramolecular oscillations arising from momentary ring formation can be extended to other groups of ketones, of which diacetyl, $CH_3.CO.CO.CH_3$, and acetyl acetone, $CH_3.CO.CH_2.CO.CH_3$, may be taken as examples. The former exhibits an absorption band similar in kind to that of acetone, but considerably displaced towards the red end of the spectrum. In this case we suppose that a double oscillation of the same type as that of acetone occurs (figs. 3 and 4)—

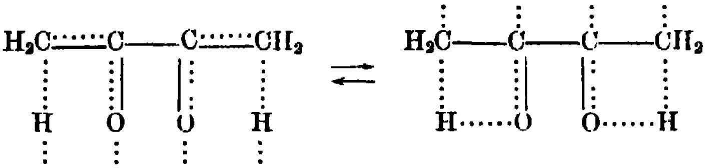


Fig. 3. Fig. 4.

while, considering the position of the band, it is also possible that an additional oscillation arising from the union and disruption of the free partial valencies of the carbon atoms of the carbonyl groups may also take place (figs. 4 and 5)—

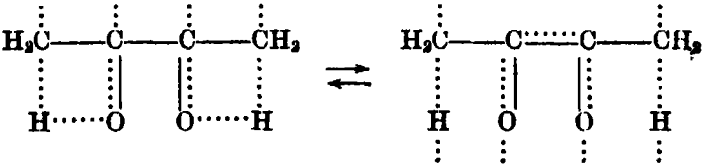


Fig. 4. Fig. 5.

The absorption band of acetyl acetone is produced in quite different concentration from that of any of the simple ketones, and therefore in all probability must be caused by a somewhat different type of intramolecular vibration. Bearing in mind that acetyl acetone exists chiefly in the enol form, and that there is evidence that the intramolecular vibrations are not due to tautomeric change, we suppose that, whilst the oscillations are in this case also due to the ultimate formation and breaking down of an unstable intramolecular ring system, the ring is different in type from that assumed to be found in the simple ketones, and that the oscillations take place between the phases represented in figs. 6 and 7.

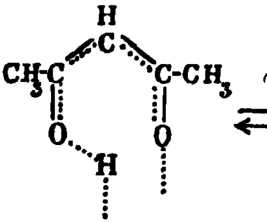


Fig. 6.

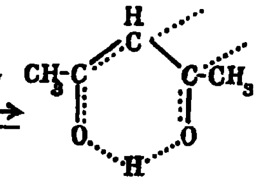


Fig. 7.

The examples quoted will, we hope, serve to make our suggestions regarding the cause of selective absorption in ketones sufficiently clear. It remains to be added that further work is in progress which is intended to test the validity of these suggestions.

Egyptian Blue.

By A. P. Laurie, D.Sc., F.R.S.E., W. F. P. McLintock, B.Sc., and
F. D. Miles, B.Sc., A.R.C.S.

(Communicated by Sir A. H. Church, K.C.V.O., F.R.S. Received October 29,—Read December 4, 1913.)

The artificial blue pigment used in Egypt from the IVth Dynasty and also used widely during the time of the Roman Empire has been investigated by many chemists, including Sir Humphry Davy,[*] Vauquelin,[†] H. de Fontenay,[‡] Darcet, F. Fouqué,[§] and Dr. W. J. Russell, F.R.S., but the exact nature of the compound and the manner of its formation do not yet seem to have been finally decided.

According to Vitruvius, the blue was made by heating together a mixture of copper filings, sand, and soda in a furnace. A great deal of information has been obtained as to the actual furnaces used and the methods of heating which will be found in "Notes on Egyptian Colours," by F. C. J. Spurrell, reprinted from the 'Archæological Journal,' September, 1895.

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[*] "On Colours in Use by the Ancients," 'Phil. Trans.," 1815.

[†] 'Passalacqua's Catalogue,' p. 239.

[‡] 'Annales de Chimie,' série 5, vol. 2, p. 193.

[§] 'Bull. Soc. des Mines de France, vol. 12, p. 36.

The temperature of the furnace was never sufficiently high to result in fusion, a mass of semi-fused frit being obtained which was easily powdered, and there is evidence that this frit was powdered and reheated more than once in order to develop the blue. Modern chemists have analysed samples of this blue, and have also made experiments on its reproduction. We do not propose to give an account of all these, but simply the summing up of the main facts which have led to the necessity for a further investigation.

Fouqué* experimented upon samples of real Egyptian blue, and gives an analysis, from which he comes to the conclusion that the blue was a double silicate of copper and calcium, for which he gives the formula $CaO,CuO,4SiO_2$, and states that the samples he examined were entirely free from soda and potash. He then proceeds to state that this double silicate is a definite crystalline compound, of which the following are the characteristics:—

"The specific gravity is 3·04.

"It is a crystalline substance, belonging to the quadratic system. It appears in the form of scales flattened parallel to the base of the prism, and often jagged at the edges, sometimes, however, ending in clear rectangular outlines. The diameter of these scales does not exceed 2 mm., their thickness rarely exceeds 0·5 mm. They are of a beautiful azure blue.

"Seen in parallel light between crossed nicols they remain tinted in all directions. In convergent polarised light they display the cross and ring characteristic of uniaxial minerals. With a quarter-wave-length mica plate it is easy to determine the negative sign of the mineral. These scales, seen under the microscope on their edge, with interposition of a nicol, offer a very remarkable pleochroism. With the rays vibrating parallel to the axis, they are of a pale rose colour; with vibrations in a direction perpendicular to the axis they are of an intense blue.

"The double refraction is 0·031."

Shortly after this paper by Fouqué, Dr. W. J. Russell took up the question of the nature of Egyptian blue, and, after examination of samples supplied to him by Prof. Flinders Petrie, proceeded to make a series of elaborate experiments on its reproduction. He has given an account of these in a paper printed in Prof. Petrie's volume on Medum, and also in a lecture read before the Royal Institution (1893). He states that he succeeded in making the blue from mixtures of copper carbonate, calcium carbonate, quartz sand, and fusion mixtures. He made a large number of experiments on mixtures in which calcium carbonate was an ingredient, and on several from which the calcium carbonate was left out. It is not quite clear whether he regarded the calcium carbonate as an essential constituent, and whether he considered that the sodium and potassium carbonates had also entered into the combination of the blue itself, or were merely there as fluxes. It is evident, on examining his notebooks, that Dr. Russell had Fouqué's paper before him, because more than once he mentions trying Fouqué's receipt, in which potassium sulphate replaces the potassium and sodium carbonates, but he in no case refers to the crystalline properties, or indicates that he has examined his samples between crossed nicols, so it would appear that he regarded Fouqué's conclusions as of no importance.

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* 'Comptes Rendus,' vol. 108, p. 325.

In the account given by Mr. Spurrell already referred to, after an elaborate description of the actual processes of manufacture as rediscovered in Egypt from the examination of remains of furnaces and of lumps of Egyptian blue that have been found, he proceeds to reject Fouqué's results, stating that his products could not be the Egyptian blue at all without soda as a necessary ingredient.

A careful study of Fouqué's paper reveals the fact that he has made several contradictory statements as to the method of preparation of the blue, and it is impossible to derive from his paper any clear conception of how the blue was made.

Our attention was directed to the matter from the fact that having got some samples of real Egyptian blue we proceeded to examine them between crossed nicols, and at once the crystalline character of the blue was revealed. The crystals were mixed with quartz and very often with a little lime, which may have been present from the beginning or may have been added as part of the mixture when the blue was used for painting. This directed our attention to Fouqué's paper, and on making a more careful examination we found that the description given by him of the crystalline character of the blue was absolutely correct.

We examined samples from the lid of a coffin of the XIth Dynasty and from a piece of Roman fresco on the Palatine Hill, a piece of the crude frit obtained from the Manchester Museum, a piece of crude frit occurring among Dr. Russell's samples, two samples from Viriconium in Shropshire, a sample obtained in Syria, and another sample formerly in the possession of Dr. Russell, from Gurob and of the XVIIIth Dynasty. In every case these samples, obtained from so many different sources and extending over such large periods of time, prove to have exactly the same crystalline character. We have also obtained a sample from Knossos, which is typical Egyptian blue.

It is evident then that Fouqué's description of the nature of this compound is correct, and it became of interest to examine the samples actually prepared by Dr. Russell to see whether they consisted simply of a semifused copper glass or of the properly constituted blue.

Fortunately Dr. Scott was able to supply us with a large number of these samples, and also to lend us the late Dr. Russell's notebooks, by which we were able to trace his methods of preparation. These methods can be roughly divided into two groups: cases in which the blue was prepared from copper carbonate, quartz, and fusion mixture alone; and from copper carbonate, calcium carbonate, quartz, and fusion mixture. The samples we obtained were all numbered and dated, so that it was possible to trace in the notebooks the processes through which they had been put. In the case of the samples containing calcium carbonate we found that in every instance they had been ground and reheated sometimes several times before the blue was properly developed, the sample after the first heating very often being black, the blue gradually improving with each new heating. In the case of the blue made without calcium carbonate the one heating seems to have been sufficient.

In all we examined some 13 specimens of the blue prepared by Dr. Russell. Of these eight were prepared with calcium carbonate and five with sodium-potassium carbonate alone. The eight specimens prepared with calcium carbonate were all genuine examples of the Egyptian blue, consisting simply of quartz grains and of the blue crystals, as far as could be detected under the microscope. Of the five samples made with sodium-potassium carbonate alone, two contained a few very minute crystals of the right formation, probably due to traces of lime, the rest consisting simply of blue glass, and therefore proving not to be Egyptian blue at all.

The enquiry up to this point had definitely established two facts. In the first place the Egyptian blue is correctly described by Fouqué as a definite crystalline silicate of copper, with the properties that have already been enumerated. In the second place Dr. Russell succeeded in reproducing this copper silicate by repeatedly grinding and heating at a temperature below fusion, a mixture of quartz, copper carbonate, calcium carbonate, and fusion mixture, but in the absence of calcium carbonate the blue was not found, with the exception of the occasional minute traces mentioned above.

At the same time it was evident that the exact conditions under which this crystalline compound was formed had not been established, and therefore the following experiments were instituted. For these experiments, the following mixture was taken: Fine sand, 36 grm.; fusion mixture, 4 grm.; copper carbonate, 8·6 grm.; calcium carbonate, 7·2 grm. The copper carbonate and the calcium carbonate are in the proportions given by Fouqué's formula. The amount of fusion mixture and of sand in this receipt is taken from one of Dr. Russell's, with the exception that the amount of copper carbonate has been slightly reduced.

The experiments were carried out in a Heræus electric resistance furnace, with a platinum-iridium junction introduced, with a view to measuring the temperature. A few grammes of the mixture were introduced into a small Battersea parting cup, which was about half full. As soon as the mixture had been heated sufficiently long to begin to set, a little piece of broken crucible was laid on the top, and the rest of the crucible packed with asbestos. The thermal junction, which was placed in a double quartz tube, but with the end of the junction bare, was buried in the asbestos, the other junction being kept at about 20°. The temperatures were read on one of Paul's thermo-galvanometers.

The sample was kept at a uniform temperature from 16 to 20 hours. The first batch inserted was kept at a temperature of 760°. On examining the product on the removal from the crucible, it was seen that the greater part of the mixture was still uncombined, but at the same time the quartz had been slightly attacked, being covered partly with a bluish-green glass. The next batch was kept at a temperature of 800°. On examining the resultant mass a considerable quantity of an olive-green glass was seen to have been formed. There was still a certain amount of white uncombined material, and a considerable quantity of black copper oxide.

The next batch was run at a temperature of 830°. On examining the product under the microscope, it contained, as would be expected, a considerable quantity of uncombined and unfused quartz, and a certain amount of black, uncombined copper oxide, the olive-green glass already described, and large quantities of the blue crystals, agreeing exactly in their optical properties with those found in the Egyptian blue in the correct samples prepared by Dr. Russell.

On cutting a section through the mass, and mounting in Canada balsam, it was quite easy to see the colourless pieces of unattacked quartz, with occasional particles of black copper oxide, and the blue crystals surrounded by a magma of the olive-green glass which was still present.

Having arrived at the temperature at which the blue was formed a gas muffle was adjusted to the same temperature, and in this larger batches were made. In the case of these batches Dr. Russell's plan of regrinding and reheating was adopted. By doing this two or three times the green glass completely disappears, and only occasional traces of black copper oxide are left, the resultant mass consisting of the blue crystals and uncombined quartz, and corresponding therefore to the lump samples of frit from the Egyptian furnaces, but much richer in the crystalline blue.

The next sample was run in the same way in the electric furnace at a temperature of 905°. This sample, on examination, proved to contain quartz, black copper oxide, and olive-green glass, but no blue crystals at all. Evidently, therefore, the temperature at which these blue crystals are formed lies between 800° and 900°, and is somewhere about 830°.

In order to confirm still further the limiting temperature of about 900° another batch was run at 890°. The product was found to consist almost entirely of green glass, with a few blue crystals at the bottom of the crucible. It is evident then from these experiments that 900° may be taken as the limiting temperature.

In a further experiment a little more of the blue frit which had been formed in the muffle furnace was taken and raised to a temperature of 1150°. It seemed to consist of quartz and bottle-green glass with no indication of the formation of cuprous oxide, as mentioned by Fouqué. When heated at the lower temperature it at once recovered its blue colour, showing the reformation of the crystalline copper silicate.

Another portion was put into a wind furnace and raised to a temperature of about 1400°, and then heated in an electric furnace at about 850°, when the blue was restored.

The matter was pressed still further by taking a small portion of the blue frit from the muffle furnace and fusing it before an oxyhydrogen blowpipe. This sample proved to contain some cuprous oxide when examined under the microscope, thus agreeing with Fouqué's description. The button was then run for 48 hours at 850°, and the result was a brilliant blue mass which, on examination under the microscope, proved to contain Egyptian blue.

These experiments, then, seem to settle conclusively the conditions as to temperature for the formation of the blue, showing that, even after raising the mass to the temperature of the oxyhydrogen blowpipe, the Egyptian blue crystallises out at a temperature of 850°.

These experiments show that the regrinding and reheating, which must have been the Egyptian practice, and which was also done by Dr. Russell, is not necessary for the formation of the blue, though it seems to be necessary in order to get the whole of the green glass converted into the blue crystalline compound. The main point of interest, however, revealed by these experiments is the formation of a crystalline silicate under conditions which, the authors believe, have not been formerly recorded.

In the first place, the mass is far below the fusion point of the whole. If the temperature is high enough, the ultimate result is to fuse the whole mass with the formation of a complex silicate, but at the temperature of 850° the quartz is attacked far below its fusing point, and this crystalline double silicate is formed, the mass merely becoming pasty in the process, never reaching true fusion, and forming when cold a frit, which can easily be crushed in a mortar, like the lumps of frit found in the Egyptian furnaces.

The next point revealed, which seems of considerable interest, is the narrow range of temperature within which this crystalline body is formed. On both sides of the region of temperature the result of the process is merely the formation of an olive-green glass, but within the right range the blue crystals are formed in the olive-green glass magma, disappearing again when the temperature is slightly raised.

The next point to be investigated was the bearing of the proportion of fusion mixture on the result. The original proportion of fusion mixture given in the formula at the beginning of the paper was taken directly from Dr. Russell's notebooks, and had been arrived at by him as the result of many experiments. Our first experiments were made with a view to finding what the effect of the increase of the amount of fusion mixture would be, and therefore a mixture was made up containing: fine sand, 15; calcium carbonate, 3·6; copper carbonate, 4·3; and fusion mixture 6 grm. instead of 2 grm. This was run for some 20 hours at 850°, the result being complete fusion into a deep green glass, the quartz practically completely dissolving in the mass.

An intermediate mixture was then taken, in which the mass of fusion mixture was reduced to 4 grm. This mixture did not fuse completely at 850° into a glass, but was heavily fritted and contained some traces of blue.

It is evident from these experiments that if the amount of fusion mixture is increased much beyond the limits described by Dr. Russell, the copper-lime silicate does not crystallise out of the mass, but remains in solution as a green glass.

The next experiment was in the opposite direction, the mixture being made up in the usual proportions, but containing no fusion mixture at all. This was run for some hours at 850°, the result being that there were indications of a slight attack upon the quartz particles, but the whole mass had refused to frit. It was then kept for a considerable time at a temperature of 1050°, the result being that, after 20 hours at this temperature, the mass was partially fritted, but contained large quantities both of cupric and cuprous oxide, and a certain amount of a yellowish-green glass. On the top of the crucible a few crystals of Egyptian blue were found. The mass was then returned to the furnace, and kept at 850° for about 48 hours. On examining it, a certain amount of Egyptian blue was found throughout the mass.

It is evident from this experiment that Egyptian blue can be formed as stated by Fouqué without the intervention of soda or potash, and is therefore evidently a compound into which neither soda nor potash enters as an essential ingredient.

A mixture was now prepared in which the amount of fusion mixture was reduced to 1 grm. After heating for 16 hours at 850°, the mass was found to be very slightly fritted, and although the quartz particles showed slight signs of being attacked, no blue had been formed. It was therefore run for some 20 hours at 1000°, the result being that the whole mass was fritted, but contained no Egyptian blue. This mass was then run for 48 hours at 850°, the result being the formation of large quantities of blue.

It is therefore evident from these experiments that the formation of the blue does not necessarily depend on the presence of soda or potash salts, but without their presence the mass is so infusible that it is difficult to get the copper, lime, and silica to enter freely into combination. When the amount of fusion mixture is only 1 grm., the temperature of 850° is not sufficient to cause proper fritting of the mass and the solution of the lime and copper, but by raising the temperature to 1000°, the small amount of soda present is compensated for by the additional temperature, with the result that on again heating at 850° Egyptian blue is freely formed.

If the amount of fusion mixture is raised to 2 grm. the best conditions are obtained, the temperature of fusion being sufficiently low to enable the mass to be fritted at 850°, while at the same time the fusion mixture is not present in sufficient excess to keep the copper-lime silicate in solution, so that it crystallises freely through the mass. If the amount of fusion mixture is increased much above this, the copper-lime silicate is kept in solution in a fused mass, and no blue is formed.

These experiments then, with those already described dealing with the conditions of temperature, define the conditions for the formation of the Egyptian blue.

As the Egyptians themselves had no pure soda to use, it seemed of interest to prepare a sample with a soda of the same composition as the Trona which comes from the Egyptian desert. A sample of soda was therefore made up containing the required impurities in the right proportions.

Analysis of Trona (probably from Wady Atrun). Given by Klaproth.*

Sod. sesquicarb.	32·6 grm.	Water and insoluble omitted.
Sod. sulphate	20·8 „	Insoluble not specified in
Sod. chloride	15·0 „	analysis.

The above mixture was introduced in place of the fusion mixture without altering the proportions of the other ingredients. On running this for about 40 hours at a temperature of 850–860°, large quantities of the Egyptian blue were successfully formed. We have also successfully prepared the blue with potassium sulphate as the flux.

For the purpose of analysis, some of the blue frit was taken which had been made in a muffle furnace, and had been re-ground and re-heated two or three times; 40 grm. were crushed, passed through a 120-mesh sieve, and then more finely ground. The finely-ground mass was then heated for three hours with aqua regia in order to dissolve out the copper oxide, and washed with water. After stirring it was found that a good deal of bluish material remained for a long time in suspension. On examination this proved to contain none of the Egyptian blue, and was therefore rejected.

The dry material, after this rough separation with water, was then mixed with bromoform of specific gravity 2·88, and treated in a centrifugal machine. After rotation, blue is found at the bottom, and a cake of lighter material at the top, which contains very little of the blue crystals in spite of a fairly deep colour. An examination of the heavy residue shows that it consists mainly of blue crystals, with a little isotropic, almost colourless glass. This glass is found in large quantities in the light material. To remove the last traces of glass the process was repeated, using a mixture of methylene iodide, and benzene of specific gravity 2·948. The material thus separated, on examination under the microscope, proved to be almost perfectly pure. It contained occasional crystals of blue, which were still united to fragments of quartz, but no glass. This material was therefore taken for analysis, and two analyses were made by fusion in the usual way with soda.

The figures obtained compare as follows with those given by Fouqué. Fouqué states that the substance is a copper-calcium silicate containing no alkali. This statement we have been able to confirm to the extent that we find it quite possible to prepare the Egyptian blue crystals without the addition of alkali at all. At the same time, it does not follow that when alkali is present some of the copper, or calcium, is not replaced by the alkali metals within the crystal.

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* Lunge, 'Sulphuric Acid and Alkali,' 1896, vol. 2, p. 61.

Fouqué's analysis is as follows:—

SiO_2	63·7
CaO	14·3
CuO	21·3
Fe_2O_3	0·6
	99·9

This analysis is, we think, somewhat open to criticism, as it is difficult to understand how, dealing with pure materials, he obtained such a large quantity of iron, especially as we found that there is no iron present at all in the blue that we have made.

The following are the results of two determinations of the silica, copper oxide, and calcium oxide:—

SiO_2	63·4	63·4
CaO	14·38	14·35
CuO	19·48	19·58

It will be noted that the figures for silica and calcium oxide agree very closely with those obtained by Fouqué, but the percentage of copper is slightly lower.

A fresh portion of the separated sample already described was treated with hydrofluoric acid, with a view to making an estimation of the alkali metals, if they proved to be present, and the results obtained are as follows:—

K_2O	1·19
Na_2O	0·93

The results add up to a total of 99·38 for our first analysis, and 99·45 for the second.

These figures seem to us to make it highly probable that, in the presence of an alkali, some of the copper or calcium is replaced by the alkali metals, and that therefore it is not correct to state that Egyptian blue consists always and entirely of copper, calcium, and silica, but this may be taken as an approximate statement of its composition, which also approximately agrees with the formula given by Fouqué—$CaO,CuO,4SiO_2$.

In addition, we have determined the two refractive indices of the crystals. The refractive index of the extraordinary ray is practically the same as that of cassia oil, 1·605(3), whilst the refractive index of the ordinary ray, determined in a mixture of monobromonaphthalene and quinoline, is 1·635(4).

This gives for the double refraction $\omega - \epsilon = 0{\cdot}031$, agreeing exactly with the figure obtained by Fouqué.

Thanks to the kindness of Dr. J. J. H. Teall, F.R.S., we were enabled to examine a sample of the blue made by Fouqué, and we found that it was optically identical with our material.

It is, perhaps, of some interest to speculate as to how this blue came to be discovered by the Egyptians, and we think the explanation is to be found in their method of glazing, which has been described by Mr. Burton in his paper on Egyptian Ceramics.*

According to Mr. Burton, their copper glaze was somewhat infusible and not suitable for running on earthenware, and it was therefore their custom to carve out of sandstone various beads and other ornamental objects, and then glaze these with a copper glaze which ran easily when in contact with a siliceous body. As has been shown by these experiments, at the lowest temperature such a glaze would be bluish green, and at a higher temperature olive green, but there would also be a certain intermediate temperature between the two olive greens in which the blue crystals of the silicate would be formed. It is therefore almost inevitable that in the process of glazing these objects carved out of sandstone, they would occasionally hit upon the temperature at which they got a deep crystalline blue, and this would very naturally lead to the attempt to prepare such a blue as a pigment by replacing the siliceous body by sand. In fact, one may say that the only change between their method of glazing on carved sandstone objects and the preparation of the blue itself was in replacing the lump of sandstone by sand, and in carefully arriving at the temperature at which crystalline blue would be formed. It is therefore easy to understand how other races who have developed the art of coloured glazing on earthenware itself have never discovered this double crystalline silicate, and how it was discovered by the Egyptians owing to the peculiar method of glazing on sandstone itself, which they seem to have been familiar with from the earliest times.

The special conditions under which this crystalline silicate has been formed seem to us to contain certain elements of novelty. They are doubtless similar to those obtaining in the devitrification which takes place when a glass is kept at a temperature below fusion for a considerable length of time, and also to the conditions present in forming Portland cement. Although it is evident that the mass contains at the temperature of 850° a certain amount of glass in a state of fusion, yet the whole mass is never fused and is therefore not disturbed in the coarse relationship of its various parts, while the process by which the blue is formed seems to be due to the fused glass acting as a carrier, dissolving the lime, copper oxide, and quartz, enabling them to combine and crystallise out, and then proceeding to dissolve further portions of these constituents.

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* 'Journ. Soc. Arts,' 3rd May, 1912, No. 3102.

If the mass is reground and reheated several times, the amount of glass that can be discovered in the finished product becomes very small, the green glass completely disappearing, and it is conceivable that if a sufficient length of time had been given to the process, a very minute quantity of glass would be sufficient to act as a solvent and a carrier, and so produce ultimately a large quantity of crystalline silicate throughout the mass, while this glass itself might possibly devitrify at a lower temperature. The final result, therefore, would be that the arrangement in bulk of the mass of material would remain the same, that the temperature would never have been raised beyond the moderate heat necessary to fuse the low fusion glass, that a large amount of crystalline silicates would result, and that the amount of glass necessary to produce this would be very small in quantity. These special conditions, therefore, for forming crystalline silicate seem to us worthy of further investigation, as they possibly have some bearing on the conditions which have occurred in Nature in certain cases.

In conclusion, we have thought these results worth publishing, not only because of their archæological interest, but because it is highly probable that there are many other crystalline silicates which can be formed in presence of excess of unfused quartz at comparatively low temperatures under these special conditions.

The Influence of the Constituents of the Crystal on the Form of the Spectrum in the X-ray Spectrometer.

By W. H. Bragg, M.A., F.R.S., Cavendish Professor of Physics in the University of Leeds.

(Received November 12,—Read November 27, 1913.)

The construction and use of the X-ray spectrometer have been described in previous papers.*

It is found that the relative intensities of the various parts of a spectrum may be greatly altered by changing the crystal which is used in the spectrometer. The present paper contains an account of experiments made to determine the origin of this effect. It is shown that it may be ascribed to well known discontinuities in the relations between the atomic weight of an absorbing screen and its power of absorbing X-rays of given quality. This cause operates through the absorbing action of the atoms of which the crystal is composed.

It is convenient, in the first place, to describe briefly the form of the spectra emitted by anti-cathodes made of various materials. In the adjoining figure are shown the spectra of osmium,† iridium, and platinum, as given by the (111) plane of the diamond. The three allied metals here show certain common characteristics. Each spectrum contains, in the first place, a quantity of

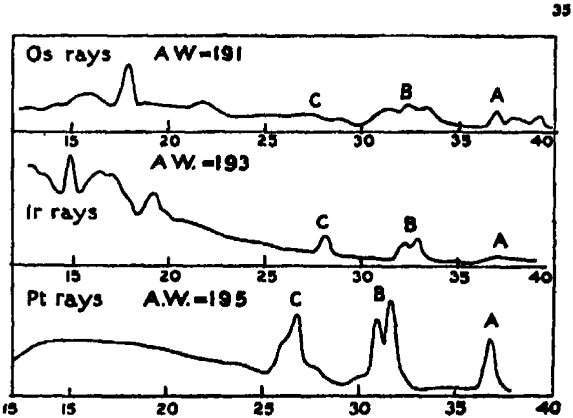

Fig. 1.

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* 'Roy. Soc. Proc.,' A, vol. 88, p. 428; vol. 89, pp. 246 and 276.

† *Note added November* 27.—A closer examination of the rays issuing from the osmium bulb shows that there are five similar triplets, the head of each being identical with one of the five platinum lines.

general radiation; radiation, that is to say, which varies continuously in wave-length over a certain somewhat indefinite range. It is clear that there is a considerable amount of such radiation for all angles of setting of the ionisation chamber which are less than about 25°. Possibly this general radiation may eventually be found to consist in part at least of bands of homogeneous rays, but the resolving powers of the spectrometer are hardly sufficient as yet to determine the point. It may be remembered that Moseley and Darwin,* using an apparatus of high resolving power, did not succeed in separating it into definite constituents. It is not, however, with this general radiation that I propose to deal at present.

Each metal emits certain groups of characteristic homogeneous rays. The characteristic rays of platinum divide themselves obviously into three groups which in the original paper† were called A, B, and C; the latter two are really double, as subsequent experiments have shown. Moseley and Darwin determined their spacings with great precision. Osmium also has three groups placed in the same way as those of platinum, but, as might perhaps be expected from its lower atomic weight, they extend somewhat further into the longer wave-lengths. The iridium spectrum again contains three groups, placed in a somewhat similar fashion to those of its companion metals, but they are not very strongly marked. Attention may be directed to the very strong peak in the osmium spectrum at 17·8°. If the spectrum had been given by rock salt (100), the angle would have been 13°.

In fig. 2 are shown the spectra of palladium and rhodium. Their remarkable simplicity and strong similarity to each other are very noticeable. The crystal used is rock salt (100). The angles at which the lines occur are, in the case of palladium, 10·4° and 11·8°; in the case of rhodium, 11·0° and 12·6°. The wave-length of the more intense palladium line is $0·576 \times 10^{-8}$, and of the more intense rhodium line $0·603 \times 10^{-8}$. As has already been explained, the precision of these lines and their remarkable intensity in comparison with the general radiation makes the rhodium and palladium bulbs of great service in the investigation of crystal structure.

Fig. 3 shows the spectra of nickel and copper. Here, again, there are two noticeable lines in each. They are of nearly equal intensity, but their relative spacings, strange to say, resemble closely those of the palladium and rhodium rays. The two copper lines are at 28·6° and 32·0°; the nickel lines at 31·2° and 34·6°. If the spectra of the last four metals are compared it is seen that the wave-length increases as the atomic weight diminishes. The frequency is not quite proportional to the square of the atomic weight.

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* 'Phil. Mag.,' June, 1913.

† 'Roy. Soc. Proc.,' A, vol. 88, p. 428.

Possibly an exact relation of this kind might have been anticipated, as Whiddington has shown that the energy of the cathode ray required to excite an X-ray of given quality is proportional to the square of the atomic weight of the metal which emits that quality, and the quantum energy of the X-ray would be proportional to the frequency.

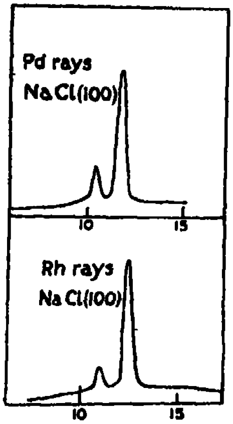

Fig. 2.

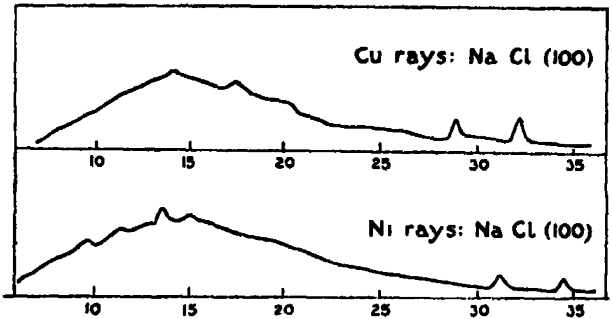

Fig. 3.

Spectra of silver and tungsten have also been obtained, but no very remarkable characteristic effects have yet been observed, except the existence of a small peak in the tungsten spectrum at 25·8.*

It should be mentioned that the form of the spectrum is influenced not only by the nature of the radiator and the nature of the crystal but also by the circumstances of its production. Characteristic rays always occur in exactly the same place, but their relative intensities with respect to one another and with respect to the general radiation are modified by such causes as the nature and thickness of the glass wall of the X-ray bulb, by the width of the slits, narrower slits giving higher resolving power, and no doubt also by the general form of the X-ray bulb, its state of exhaustion, the nature of the coil, and so forth. The spectra which are shown above are therefore examples made under circumstances which need special definition before they can be fully interpreted. It is only the positions of the various peaks representing the wave-lengths of the characteristic rays which are invariable.

The spectrometer furnishes us with an arrangement of radiations in the order of the magnitude of their wave-lengths, and we are therefore able to make measurements on the relation between the wave-length and the absorbing powers of various screens.

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* 'Roy. Soc. Proc.,' vol. 89, p. 247.

From the work of Barkla we can anticipate the broad results of such measurements. In papers published at various times Barkla has shown that each metal emits characteristic homogeneous rays, and that the rays characteristic of any one metal can only be excited by rays characteristic of metals of higher atomic weight than its own. This is at least true as long as we deal with waves of one series as defined by Barkla. He has also shown that homogeneous X-rays are strongly absorbed by any substance in which they can excite the rays characteristic of that substance. If, for example, we consider the absorption of rays by a nickel screen we find that the absorption coefficient diminishes as the rays which we are considering are characteristic of chromium, iron, cobalt and nickel successively. Nickel itself is peculiarly transparent to its own rays. None of these substances are able to excite the characteristic X-rays of nickel; but if we pass on now to consider the absorption coefficient of nickel for the rays emitted by zinc, we find a sudden and very large increase. From this point onwards the absorption coefficient is of a higher order altogether, and though it again declines as the atomic weight of the radiator increases, it is evident that the coefficient has at a certain critical stage mounted to a much higher range of values. These facts are perhaps more easily expressed in terms of the results of the X-ray spectrometer, and it will be shown in a moment that the new experiments quite confirm them.

Let us for example suppose that we had an X-ray spectrum in which the energy was so distributed among the various wave-lengths that the form of the spectrum was the straight line AB in fig. 4. Now let us imagine ourselves placing in turn various absorbing screens in the path of the rays and remeasuring the spectrum in each case throughout its entire length. The abscissæ in this figure are the angles of the ionisation chamber for rock-salt (100). The spectrum obtained after the insertion of a copper screen would be something of the form of the line marked "Cu" in the figure; for whereas copper rays are themselves (see fig. 3) emitted at angles 28·6° and

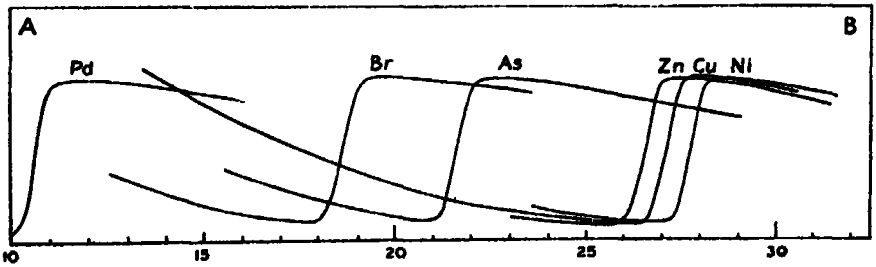

FIG. 4.

32°, these we know from Barkla's work must belong to the region of wave-lengths which are transmitted with particular ease, inasmuch as they cannot excite the characteristic radiations of copper, but for wave-lengths somewhat smaller than this we should expect a very marked increase in the absorption coefficient of copper, and this would be indicated by the sharp drop of the curve in the figure. The subsequent slow rise as the wave-length further diminishes is meant to represent the fact that after this stage has been passed the absorption coefficient once more diminishes with the wave-length.

Let us now proceed to consider actual experimental results. We cannot obtain a spectrum of the simple form of fig. 4, but we may use, for example, an osmium spectrum in which are represented waves of a large range of wave-length, though they may not all be represented to the same extent. In fig. 5 are shown the spectrum over a range between 25° and 30°, when zinc, copper, iron screens are successively placed in the path of the osmium rays. Zinc is transparent in the higher order to practically all the wave-lengths within these limits. Copper is transparent in the higher order only to waves past 27·5°. The insertion of the copper screen has removed an important radiation at about 27°, transmitting easily the radiation of 28·5°. Iron is not transparent in the higher order to any wave-length within this radiation.

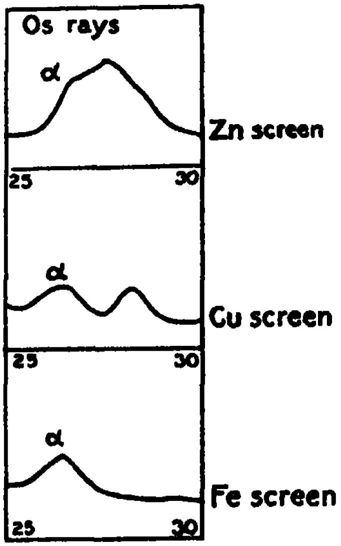

Fig. 5.

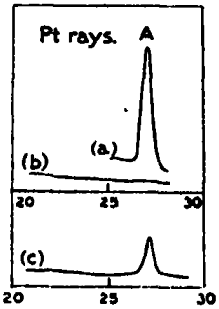

Fig. 6.

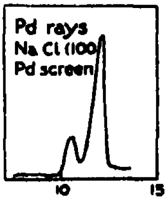

Fig. 7.

The peak marked α appears in all three, but this is as it should be, for it is the second order spectrum of the strong osmium band at 13° and possesses the penetrating power of that band. The penetrating power of the band at 13° is high because the wave-length is small. Though it lies on the wrong side of the critical points of the zinc, copper, and iron curves of fig. 5, it is far distant from those points. The same effect may be shown by the use of the rays from a platinum bulb. The platinum rays have a strong peak at 27°, which I have termed A on previous occasions. The figure (fig. 6) shows the spectrum of platinum between 20° and 30°, first when no screen is placed in the path of the rays, secondly when a zinc screen is placed in the path of the rays, thirdly when a copper screen is interposed. The figure shows that the zinc is relatively opaque to all rays at smaller angles than 27°, but transmits easily the strong radiation at that angle. Copper, however, is opaque to rays at 27° also. Thus the division between relative transparency and opacity is sharply marked; an atom of weight 65 transmits rays at 27°, and an atom of weight 63 does not. The same effect is illustrated again in fig. 7, which shows the effect of placing a palladium screen in front of the rays from a palladium bulb. It will be observed that, while the palladium rays themselves are transmitted in considerable quantity, all the rays to the left of the 10° are very largely absorbed.

Let us now pass on to consider what happens when the atoms in the crystal itself are such as to be relatively opaque to portions of the incident radiations. Fig. 8 (*c*) shows the spectrum of platinum rays reflected by a crystal of zinc blende. If we compare this with the form of the spectrum as given by rock salt (fig. 8, *a*), we observe that the peak A is very largely increased relatively to the peaks at B and C. From what has preceded a very simple explanation is at once forthcoming. The rays at 27° (in NaCl, or 24° in ZnS) which constitute the A peak penetrate the zinc with comparative ease; the rays at 23° and 19° (about 20° and 17° in ZnS) are very quickly absorbed by the zinc; consequently there is little opportunity for their energy to be scattered or reflected, since the great bulk of it is quickly taken up in other ways. These other ways we know from previous experiments to be wholly or at least in great part the conversion of X-ray energy into cathode ray energy. When the quality of the X-ray is such as to be able to excite the characteristic radiation in a substance on which it falls, there is at the

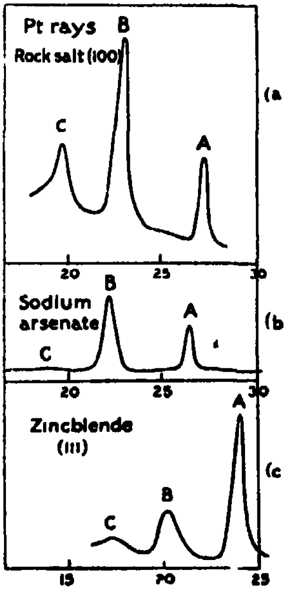

FIG. 8.

same time an unusually large expenditure of energy in the production of cathode rays.

An experiment such as that shown in fig. 8 (*c*) above may be taken to indicate therefore that the scattering which is the basis of the reflection of X-rays does not display the same marked change as the absorption coefficient does on passing through the critical value. Zinc blende gives a very large reflection of the peak A because the zinc is relatively transparent to the rays at 27°. In this region of the spectrum much less energy is spent in making cathode rays and there is much more available for reflection. There is no evidence as yet that the magnitude of the A peak as given by zinc blende is due to any special response of the zinc to the rays at that point; the effect is simply explained as a consequence of the peculiar absorption laws. We may test this hypothesis further in the following way. If we take crystals which contain an atom whose weight is somewhat larger than that of zinc we ought to find that the line of division between relatively high transparency and absorption has moved towards the left into the radiation of smaller wave-lengths. In fig. 8 (*b*) is shown the spectrum of the platinum rays given by a crystal of sodium arsenate. Here it will be seen that both the peaks A and B are now strongly represented, but C remains still very small. The reason is that arsenic absorbs strongly all rays to the left of about 22° when the spectrum is given by NaCl (100); this is equivalent to about 21° in sodium arsenate. A crystal containing bromine, such as potassium bromide, allows rays to pass through which are short enough to include all the three groups of platinum or osmium. In the figure (fig. 9) is shown the spectrum of the osmium rays given by potassium bromide and the three groups are now shown more nearly in their proper proportions. There should be a strong peak at 10·5°, namely, that which occurs in the rock salt (100) spectrum at 13°, as has been mentioned already. This is almost completely destroyed in the present spectrum, for bromine is relatively opaque to the rays of that quality.

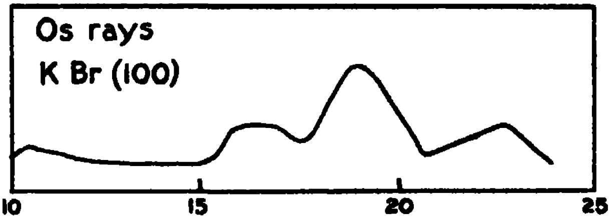

FIG. 9.

The main result of these experiments is to show the influence of the weight of the atom in the crystal on the form of the spectrum. Within a region of atomic weight from 40 upwards, certain remarkable discontinuities of absorption occur in the manner explained above. When such atoms are present therefore in the crystal and the radiations divide themselves between those which lie on the one side of a critical point and those which lie on the other side, the spectrum will also show a sharp division at that point, being far stronger relatively on the one side than on the other. As to the influence of the weights of the atoms in a crystal when they are smaller than 40, we have still to take into account the very remarkable change in their absorption coefficients to all X-rays which occur when we pass from atoms of carbon and oxygen and so forth to atoms of aluminium or chlorine. Barkla has shown that aluminium absorbs all X-rays nine times as much as carbon, weight for weight. If the scattering power does not vary in the same abnormal way, then we should expect that a crystal of small atomic weight would be an exceptionally good reflector, on the same principle as before, that the less energy spent in absorption, the more there is available for scattering. We should expect, therefore, the diamond to give strong reflections apart from other reasons. This is well known to be the case. The diamond, moreover, gives reflections at far larger angles than other crystals. It must go a long way to explain this, that the spacings of the planes in the diamond are small, and therefore the spectra are thrown to wider angles, and also, that in a case where so much energy is spent in reflection, second-order spectra will be more obvious. It is quite possible that thermal agitation may have less influence on reflection intensity in the case of the diamond than in the case of other crystals, but these experiments show that good reasons for the peculiarities of the diamond reflection are already to be found in other directions.

It is very important to know the exact nature of the law connecting the atomic weight with the amount of scattering. The above experiments show that there are not the same abnormal variations in the amount of scattering as we proceed from lower to higher atomic weights as there are in the case of the absorption coefficients. Certain experiments which have been made by my son and myself indicate that the law is one of simple proportionality; that is to say, the amplitude of the scattered wave is proportional to the weight of the scattering atom. At any rate, certain results, to which I will now refer briefly, are very simply explained on this hypothesis.

A structure of the diamond, founded on measurements made with the X-ray spectrometer, has been explained in a recent paper.* It was pointed out that the second-order spectrum given by the (111) plane disappeared in consequence of the peculiar spacing of the planes. Zinc blende has the same construction as the diamond, except that the two interpenetrating lattices are composed of zinc and sulphur atoms respectively, and are therefore of different weight, while the two lattices of the diamond are both composed of carbon atoms, and are therefore of equal weight. The disappearance of the second-order spectrum referred to may be considered as due to an interference between the effects of the two lattices. When these two lattices are no longer of equal weight, the interference is incomplete, and accordingly the (111) spectrum of zinc blende gives a small second-order spectrum.

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* 'Roy. Soc. Proc.,' A, vol. 89, p. 277.

In the case of fluorspar, the first order spectrum of the (100) planes and the second order spectrum of the (111) planes have again disappeared, or very nearly so. In this case there are three lattices. The two fluorine lattices can be derived from the calcium lattice by equal simple translations in opposite directions along a cube diagonal; the amount of translation being a quarter of the length of the diagonal. The result is that the (100) planes contain calcium atoms and fluorine atoms alternately. There are two fluorine atoms to one calcium atom and therefore the weights in the planes are approximately equal, as in the case of the diamond. The disappearance of the first order spectrum indicates, therefore, that the conditions for mutual interference are satisfied when the weights are nearly equal, independently of the fact that in the one case the weight is due to calcium atoms and in the other to twice as many fluorine atoms. Weight alone and not atomic nature has determined the amount of scattering. The disappearance of the second order (111) spectrum is explained in the same way.

Other illustrations of the proportionality between scattering power and atomic weight are to be found in a comparison of the spectra of the various members of the calcite series. This point, with its bearing on the analysis of crystal structure, is more fully considered in a separate paper by W. L. Bragg.

Mr. W. L. Bragg and Mr. S. E. Peirce have kindly helped me to make some of the measurements referred to in this paper.

A Simple Form of Micro-Balance for Determining the Densities of Small Quantities of Gases.

By F. W. Aston, B.A., B.Sc., A.I.C., Trinity College, Cambridge.

(Communicated by Prof. Sir J. J. Thomson, O.M., F.R.S. Received November 13,—Read December 11, 1913.)

In some work on the homogeneity of atmospheric neon it was desirable to adopt a method of determining gaseous densities which could be easily and quickly performed with a very small volume of gas without risk of loss or contamination, and which in addition would yield results reliable to about 0·1 per cent.

The standard method of weighing a known volume of the gas on an ordinary balance yields results of the highest accuracy so long as that volume is large enough. As 0·01 mgrm. may be regarded as the ordinary limit of accuracy of the chemical balance at least 10 mgrm. of the gas would be required, and even if this quantity (rather more than 10 c.c. at atmospheric pressure in the case of neon) had been available, the elaborate precautions necessary to obtain 0·1 per cent. accuracy would put the method out of court on the consideration of time alone.

On the other hand the ingenious method devised by Schloesing[*] could hardly be expected to give results of this accuracy, and is also open to objection on the score of contamination.

Inasmuch as the accuracy of determination of the density of a very small quantity of gas must ultimately be limited by the sensitivity of the balance employed, it seemed to me that the most hopeful solution of the problem was offered by the quartz micro-balance first described by Steele and Grant[†] and subsequently used with such notable results by Gray and Ramsay[‡] in their determination of the density of radium emanation.

This instrument, which can be made of a sensibility of 10^{-9} grm., was made with a small quartz bulb fixed to one end of the beam, the weighings being done by altering the pressure of the air in the balance case. By knowing the buoyancy of the bulb and observing the pressure necessary to bring the beam to zero, the weight at the other end of the beam could be calculated. If, however, we alter this procedure and balance the bulb by a *fixed* counterpoise, the pressure necessary to bring the beam to zero will be a

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[*] 'Comptes Rendus,' 1898, vol. 126, p. 220 and 476.

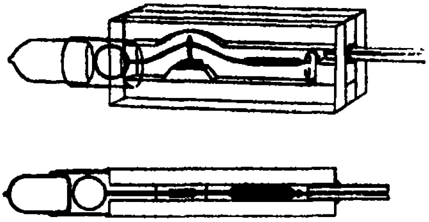
[†] 'Roy. Soc. Proc.,' 1909, A, vol. 82, p. 580.

[‡] 'Roy. Soc. Proc.,' 1910, A, vol. 84, p. 536.

measure of the density of the gas in the balance case. This is the principle of the method here described.

It will be seen at the outset that the balance is used as a truly null instrument, all the forces on the beam, with the single exception of surface pressure, being identically the same whenever a reading is taken, so that the most sweeping simplifications may be made in its construction.

The general arrangement of the instrument can be seen in the accompanying diagram, which shows it in plan and elevation.



View and Plan of Balance and Case, about half actual size.

The moving part of the balance is made entirely of fused quartz (shown black). It turns upon a single knife-edge cut on a piece of quartz rod about 0·5 mm. thick. The one on the balance at present in use was ground for me by Messrs. Hilger, but very satisfactory ones can be made by the method given by Steele and Grant (*loc. cit.*).

To this rod, a few millimetres above the knife-edge, are fused two others of about the same thickness forming the arms of the beam. To the end of one arm is fused a quartz bulb and to the other a counterpoise made of a piece of rod about 2 mm. thick.

The quartz rods and bulb were supplied by the Silica Syndicate, Ltd., the latter had a volume of about 0·3 c.c., and as the density of air is negligible compared to that of quartz, it was sealed up without exhaustion.

The assembling of the beam was done by means of a small oxy-coal-gas flame, and proved a surprisingly easy operation, the one in use at present being made and roughly adjusted in a quarter of an hour. It has a total length of about 5 cm., and weighs under 0·2 grm.

Adjustment of the Balance.

This is done in two stages, the first consists in bending the arms and adding or subtracting small quantities of quartz to or from the counterpoise until the whole swings evenly when supported on the knife-edge in the open air, and has a fairly long period of swing. This operation is also much easier than would appear at first sight, for fused silica lends itself particularly well to this kind of work.

The fine adjustment is, however, a much more troublesome operation, as in this the balance can only be tested at about the pressure at which it is required to work. It is obvious that, given sufficient sensitivity, the smaller the working pressure in the balance case the less the quantity of gas required for a measurement. On the other hand, as an accuracy of 0·1 per cent. was desired, it was decided to employ a pressure which could be measured to that degree without elaborate apparatus, in practice about 100 mm. of mercury.

For this adjustment a rough balance case was made of a piece of glass tube closed at one end by an accurately fitting rubber stopper, which could be easily removed to admit the balance. Inside the tube was a piece of plane quartz mounted horizontally on a piece of sealing-wax to support the knife-edge. The other end of the tube was connected to a mercury manometer and, by means of a three-way tap, either to the atmosphere or to a reservoir kept exhausted by means of a filter-pump.

The procedure was quite simple. The roughly adjusted beam was taken, and a small excess of quartz added to the counterpoise; it was then placed in the tube and the latter exhausted, and the pressure at which the balance turned over observed. If this was too high, the end of the counterpoise was drawn out into a thin tail; if too low, the end of this tail was allowed to fuse up into a knob. The latter adjustment was invariably the final one, as by this process, if the time of immersion in the flame is judged with care, the C.G. of the balance can be moved towards the bulb with the greatest possible delicacy.

In general, the sensitivity of a balance can be conveniently judged by observing its period of swing, but, in this one, so large is the surface of the bulb in relation to the whole moving mass that the latter is nearly perfectly dead beat, so that its sensitivity is best measured by observing, by means of a microscope, the movement of the tail corresponding to a definite small change of pressure. The actual adjustment for sensitivity is carried out by adding or subtracting minute quantities of quartz to or from the top of the rod carrying the knife-edge, which is left projecting for that purpose.

After every trial air must be admitted, and the balance taken out and readjusted, and as the greatest care must be observed not to damage the knife-edge during so many manipulations this "vacuum" adjustment puts a somewhat severe tax on one's patience. It can usually be completed in an hour or so, after which the balance is thoroughly annealed and cleaned by the methods recommended by Steele and Grant (*loc. cit.*).

The Balance Case.

This is made of pieces of glass cemented together with sealing-wax as indicated in the figure. In order that the quantity of gas used might be as small as possible, the narrow part of the balance, *i.e.* all but the bulb, is contained in a cell about 3 mm. wide, made of thick plate glass, and in order to cut down the volume still further a portion of the upper side is cut away, as indicated, to make room for the highest central part of the beam. The bulb is housed in a glass tube, which in its turn is closed by a glass plug with a flat face pushed in as far as possible without actually touching the bulb itself.

The plane upon which the knife-edge rests is a small piece cut off a parallel quartz plate (ground by Messrs. Hilger) and cemented on to a glass support which rests on the bottom of the cell. Owing to its very small dimensions, a few square millimetres, the adjustment of this plane to an accurately horizontal position appeared, at first sight, to present some difficulty. This, however, was easily surmounted by the following very simple device:—

Two small plumb-bobs were suspended by pieces of white thread behind the balance case at such a distance apart that they subtended about a right angle at the quartz plane. The thread of one of the bobs was then observed together with its mirror image in the quartz plane from a point a few inches above and in front of the latter, and the whole balance case tilted until the two lay exactly in one straight line. This was repeated with the other bob, and when both satisfied this condition the balance was permanently fixed in position. It is clear that, subject to the sides of the cell being optically good, the plane must now be truly horizontal.

The balance case is connected by a short piece of capillary tube, as a precaution against an accidental destructive inrush of gas, through one stopcock to the gas-admission apparatus and pump, and through another to the short limb of the manometer.

This is of the simple U-form, the two limbs being made of tube of identical diameter (about 1 cm.). The longer limb is exhausted as highly as possible and sealed off. The level of the mercury in the U is accurately controlled by the pinchcock and squeezer device described by Lord Rayleigh.* The reading of the difference of level is done by means of brass sleeves, as in the ordinary barometer, the one carrying a scale and the other a vernier reading to 0·05 mm.

When the balance is not in use the case is kept completely exhausted, the uptilted tail lying in the upper of the two small quartz forks fixed inside the case, in the position shown in the diagram.

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* 'Phil. Trans.,' A, vol. 196, p. 211.

As a precaution against draughts or other exterior disturbance, the whole balance case is surrounded with a lead box, which also contains a thermometer reading to 0·1° C.

The balance case, the manometer, and the tubes through which the gas was admitted had a total volume of only a few cubic centimetres, so that *the quantity of gas necessary to make a determination amounted to* 0·45 *c.c.* in the case of oxygen.

Method of Taking Measurements.

About the right volume of gas, generally known from previous experience, is admitted into the balance case and manometer, and the mercury level in the latter slowly raised (increasing the pressure in the balance case) until the bulb rises and the knob at the extremity of the counterpoise appears on the field of a fixed reading microscope. The pressure is then carefully adjusted, by means of the squeezer, until the knob reaches some definite arbitrary zero point, and shows no tendency to move. The pressure is then read off. The gas is now pumped out and the operation repeated with a gas of known density, the ratio of the densities being clearly the inverse of the pressures read.

Behaviour of the Balance in Practice.

The instrument was primarily designed to compare the densities of specimens of neon. The bulb has a buoyancy corresponding to 0·3 c.c. This volume of neon at a pressure of 100 mm. weighs about 0·04 mgrm.; hence to give an accuracy of 0·1 per cent. the balance must be sensitive to 0·00004 mgrm. There is, however, not the least difficulty in obtaining ten times this sensitivity.

The distance from the knife-edge to the knob at the end of the counterpoise is about 3 cms. The reading microscope has an eyepiece scale of 40 wide divisions to the millimetre. In the case of oxygen the knob of the balance now in use moves 30 microscope divisions for a change of pressure of 1 mm. in the manometer. So excellent is the definition that a change of position corresponding to 0·05 division could easily be detected, this implies a sensitivity of 10^{-6} mgrm., about the same as that attained by Steele and Grant.

When the gas is let into the evacuated balance case, the tail generally tends to stick in the fork; the pressure must then be raised rather above that which should be sufficient and the floor of the room lightly tapped with the foot. This is the only form of release as yet found necessary.

The damping due to the volume of the bulb has already been mentioned, it is quite marked in the open and is increased very greatly by the close-fitting walls of the balance case. This constitutes one of the greatest virtues of the instrument, as not only does it mean that the tail follows change of pressure with admirable fidelity, making the setting rapid and easy, but since it is literally impossible to make the beam move rapidly enough to do itself an injury it will suffer the most incredible ill usage, and in addition give accurate results under very unfavourable conditions as regards vibration. Thus the one at present set up on an ordinary laboratory table will give quite satisfactory readings even while two liquid air machines and a large gas engine, etc., are running in the next room.

The only serious fault of the balance is the tendency of the zero to alter. When the first one was set up this was so pronounced as to render the instrument quite useless, as it was out of all proportion to the sensitivity: New beams, planes, and knife-edges were tried and radioactive matter introduced to eliminate electrostatic effects with little or no result, and, in despair, the thing was left to itself (in an evacuated state) for several days. On trying it again the disturbances had almost disappeared, and a week or so later the zero could be trusted to remain constant for a reasonable time.

This effect has not yet been satisfactorily explained, but I am inclined to put it down to actual distortion of the beam due to insufficient annealing, the effects being much more serious than those noticed by Steele and Grant on account of the more rigid construction of their beam.

The Influence of Temperature.

In the measurement of density by the ordinary method, temperature and its exact measurement play an important part. The density globe must remain for a long time in a bath of known temperature before it is detached from the manometer, and should hang, for hours if the highest accuracy is desired, in the balance case before its weight is determined. By the present method these delays are entirely eliminated, for so minute is the quantity (about 0·0005 grm.) of gas employed that when this is compressed inside the massive walls of the balance case thermal equilibrium is almost instantaneous. *The whole operation of determining the density of a gas to* 0·1 *per cent. can be completed in* 10 *minutes* (this time including that necessary for admission and subsequent exhaustion of the gas).

Such speed makes the temperature correction for zero quite unnecessary, as it is safer to take a reading with the standard gas either before or after a set of measurements is made, during which the temperature of the balance-case never alters enough to affect the fourth place in the results. This check also eliminates any error due to the creeping of the zero already alluded to.

Oxygen derived from potassium permanganate and purified over potash and phosphorus pentoxide was adopted as the most convenient gas for standardising purposes. Pure dry air also was used, comparisons between the two serving to show how reliably the balance was working. In some cases, however, such as the comparison of the densities of several samples of the same gas for purity, the standard gas is not required, as for this purpose the readings of pressure are themselves quite sufficient.

The following are a few typical readings for oxygen and air, together with the density of the latter derived from them if O = 16 :—

Oxygen	65·20	75·65	76·00	76·35
Air............	72·00	83·45	83·90	84·35
Density	14·49	14·50	14·49	14·48

The density from the accepted values, after proper corrections have been made, works out at 14·482.

As the working pressure is low, correction must be made in order to obtain the weight of a standard litre at N.T.P.; but, on the other hand, the molecular weight is given directly by comparison with the result for oxygen. Thus the following figures were obtained at the same time as were those in the last column given above, they are the pressure readings for seven different fractions of very highly purified atmospheric neon :—

121·05, 120·25, 121·05, 120·90, 121·00, 121·05, 121·05.

The mean is 121·00. This, compared with 76·35 as above, gives a density of 10·096 (O = 16), and therefore a molecular weight of 20·19, which agrees to practical identity with the accepted value of 20·200 obtained by Watson.*

It is as well to note here that the only theoretical correction necessary to apply to the instrument is the one described by Lord Rayleigh for change of buoyancy of the bulb with change of pressure. Here the maximum change is some 50 mm., and, as the bulb is enormously more massive for its dimensions than the ordinary glass density globe, this correction could not possibly affect the fourth place in the result.

The results quoted above show that, used in the work for which it was designed, the apparatus is entirely satisfactory, and it seems likely that, by further refinements in construction, its efficiency could be considerably extended. Thus there is, theoretically at least, no definite limit imposed upon the quantity of gas necessary to "float" the bulb. This indeed bears no obvious relation at all to the quantity required to fill it—one of the great advantages obtained by weighing by displacement—so that by shaping the balance case, more closely to the balance, the necessary quantity of gas could be still further diminished.

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* 'Chem. Soc. Journ.,' 1910, Trans., vol. 50, p. 810.

Again, clearly, if larger quantities of gas are at disposal, the instrument could, with much greater ease in its construction, be arranged to work at atmospheric pressure, the accuracy being thus at once extended to the fifth place.

In addition, it seems likely that it may be turned with profit to another problem, viz., the measurement of pressure in gases of known density, Readings with the present instrument show that it has an even scale over comparatively large displacements, so that it could easily be adjusted to read pressures of, *e.g.*, 0 to 2 mm. with an accuracy of about 0·01 mm. There is nothing in its construction which precludes its being made *entirely* of quartz and glass, so that it offers a hopeful solution to the problem of observing the phenomena of electrical discharge at low pressures in gases, such as the halogens, which debar the use of mercury manometers. As in this case the volume would not have to be curtailed, a larger bulb might be employed, and the reading microscope replaced with advantage by a mirror and scale.

In conclusion, I may state that the instrument herein described may be assembled in a comparatively short time by any skilled glass-worker, and, thanks to the very small quantity of material used, at a cost of a few shillings.

Summary.

1. A simple micro-balance is described, by which the densities of gases may be determined relative to some standard gas, using a null method.

2. About half a cubic centimetre only of the gas is required.

3. The determination can be performed in a few minutes, with an accuracy of 0·1 per cent.

4. Possibilities of its use in other fields of research are indicated.

On a Second Spectrum of Neon.

By THOMAS RALPH MERTON, B.Sc. (Oxon.).

(Communicated by Prof. G. D. Liveing, F.R.S., and Sir J. Dewar, F.R.S.
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The spectrum of the gases of atmospheric air which were not condensed at the temperature of liquid hydrogen was first investigated by Liveing and Dewar,[*] who found a large number of lines which did not belong to the spectra of hydrogen or helium. The spectrum of the glow from the negative pole was photographed, owing to the fact that the secondary spectrum of hydrogen was predominant in the capillary.

It was found that, whilst the secondary hydrogen spectrum disappeared when a jar discharge was used, the greater part of the lines of unknown origin were also obliterated.

Stassano[†] has enumerated about one hundred lines of the spectrum of the aurora, from the results of different observers, two-thirds of which he has found to be identical, within the limits of experimental error, with the lines of unknown origin recorded by Liveing and Dewar.

Neon in a state of great purity was subsequently prepared at University College, London, and its spectrum was measured by Baly,[‡] who observed that the spectrum was not appreciably altered when the discharge from a Leyden jar and spark-gap was used.

Five years later the spectrum was again measured by Watson,[§] who confirmed the measurements of Baly, and added a considerable number of lines which had not been previously observed. Watson was unable to find any trace on his plates of a large number of the lines found by Liveing and Dewar (*loc. cit.*), and no satisfactory explanation for the origin of these lines has been found.

In the present investigation I have examined the spectra obtained under different conditions with two vacuum tubes which had been filled at University College with neon, which was presumably as pure as that used by Watson and Baly. No trace of any impurity could be detected in the spectrum from the capillary, though the hydrogen lines could be faintly seen in the glow around the electrodes.

The spectra were photographed with a large Hilger wave-length spectroscope with a camera attachment, and with a grating spectrograph having a 1¼ inch concave grating of 4 feet radius, ruled with 20,000 lines to the inch. The latter instrument had the advantage of a high dispersion and consequently increased accuracy, with the disadvantage that long exposures of upwards of 10 hours were required to obtain satisfactory photographs.

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[*] 'Roy. Soc. Proc.,' 1900, vol. 67, pp. 467–474.

[†] 'Ann. de Chimie,' 1902, vol. 26, p. 40.

[‡] 'Phil. Trans.,' 1903, A, vol. 202, pp. 183–242.

[§] 'Roy. Soc. Proc.,' 1908, vol. 81, pp. 183–194.

A comparison was made of the spectra obtained with a weak discharge from an induction coil (equal to about a half-inch spark in air) and with the same discharge when a small Leyden jar and a spark-gap of about 2 mm. were used. The intensity of the discharge was not great enough to bring out any lines due to the electrodes or the glass walls of the capillary. The neon tubes, which are known to deteriorate, were not at all rapidly destroyed by the strength of the discharge used.

With the jar discharge the lines of the ordinary neon spectrum in the red and orange were much weaker, but no new lines could be detected. In the more refrangible region, however, the spectra were entirely different, consisting of a large number of lines which were not present in the ordinary neon spectrum, while the strongest of the ordinary neon lines were only just visible. The most refrangible rays measured, having wave-lengths 3218 Å.U. and upwards, must have been of very considerable intensity, since they had to pass through the glass walls of the capillary.

The wave-lengths of most of these lines have been measured from photographs taken with the grating spectrograph, using the helium lines as standards, but some of the lines in the green were so feeble that this was not possible, and their wave-lengths were accordingly measured with an accuracy of ±1 Å.U. from photographs taken with a very long exposure on the prism spectrograph.

A comparison of measurements made on three plates shows that the differences between the mean wave-length and the least concordant measurement are on the average 0·04 Å.U. In a few of the fainter lines, however, which were also somewhat diffuse, the differences were as great as 0·1 Å.U. (and in one case 0·12 Å.U.). The measurements are therefore given to five significant figures, the probable error being less than 0·1 Å.U.

In the following table are given the wave-lengths of the lines, together with their intensities expressed in the usual way on an ascending scale from 1 to 10. In the third column are given the corresponding values found by Liveing and Dewar, and in the fourth the values of lines which possibly correspond, given by Watson. The latter only correspond in a few cases, the strongest lines in the ordinary spectrum being feebly visible in the new spectrum. The red yellow and yellow green lines which occur in both spectra have not been included in the list.

Wave-length.	Intensity.	Living and Dewar.	Watson.
4431·2	2	4431	
4428·9	3	4429	
4413·5	2	4413	
4409·6	3	4409	
4398·2	2	4398	
4392·3	3	4392	
4379·8	2	4380	
4290·7	0	4290	*
4250·9	0	4251	*
4233·9	1	4234	
4231·9	1	4232	
4220·0	3	4220	
3856·8	0	3856	*
3830·0	4	3830	
3818·6	2		
3800·2	1	3800	
3777·3	5	3777	
3766·5	5	3766	
3754·0	2	3754	3754·32 (3)
3751·5	2	3751	
3735·1	3	3735	
3727·3	6	3728	
3713·3	9	3713	
3709·8	5	3710	
3701·9	0	3703	3701·31 (5) ?
3694·4	9	3694	3694·38 (0)
3664·3	7	3664	
3645·1	2	—	} (Double L. and D.)
3644·2	3	3644	
3628·2	1	3628	
3612·6	0		*
3594·4	2	3593	
3593·8	2		
3574·9	6	3575	
3574·5	0		*
3571·5	3	3571	
3568·7	8	3569	
3566·1	2		
3561·4	2	3561	
3558·0	2	3558	
3543·1	4	3543	
3520·7	4	3521	3520·61 (9)
3515·4	1	3515	3515·32 (5)
3503·8	2	3504	
3482·2	4	3482	
3481·0	0	3481	*
3477·9	0		
3472·8	0	3473	3472·68 (6)
3459·5	0	3460	
3456·8	2	3456	
3455·0	0	—	*
3453·3	0	—	*
3447·9	2	—	3447·83 (5)
3428·9	1	3429	
3417·9	2	3418	3418·03 (5)
3417·1	1	3417	
3413·6	0		*
3407·2	1	3407	
3405·1	0	3404	*

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* These lines were measured on one plate only. Lines of intensity 0 were just visible, and could only be measured with difficulty.

Wave-length.	Intensity.	Liveing and Dewar.	Watson.
3393·0	3	3393	
3388·7	3	3388	
3378·5	4	3378	3378·27 (? 0 Watson.)
3372·1	0	3372	*
3367·5	3	3367	
3360·9	3	3360	
3355·2	6		
3346·1	0	—	*
3345·7	2	3345	
3344·6	3	3344	
3335·1	7	3335	
3329·4	2	3329	
3327·4	3	3327	
3324 0	4	3324	
3320·0	1	3319	
3298·0	1	3297	
3218·5	1	3218	

* These lines were measured on one plate only. Lines of intensity 0 were just visible, and could only be measured with difficulty.

The following lines were too weak to be measured with the concave grating spectrograph and were measured from photographs taken with the prism spectrograph :—

Wave-length.	Liveing and Dewar.	Wave-length.	Liveing and Dewar.
5036	5038	4369	4370
4627	4628	4290	4290
4615	4616	4257	4258
4568	4570	4250	4251
4521	4523	4240	4241
4498	4500	4217	4218
4468		4151	4151
4456	4457	4134	4134
4438	4438	4099	4099
4420		3945	

A comparison of the wave-lengths found with the tables of Liveing and Dewar shows that nearly all the lines measured agree with the values given by them, very few being absent from their tables, and these being (with one exception) lines of very small intensity. On the other hand, about 50 per cent. of the lines given by Liveing and Dewar have not been found. This may be due to some differences in the spectra from the wide part of the tube and the capillary, but more probably to the fact that the illumination with the concave grating used in the present investigation was far less than with the calcite prism spectrograph used by Liveing and Dewar. There can be little doubt, however, that the lines in question correspond, and there is no systematic agreement between the wave-lengths of the lines found and those of any probable impurity.

It would appear, therefore, that neon, like argon, krypton and xenon, is capable of giving two different spectra according to the manner in which it is electrically excited.

I should like to express my sincere thanks to Sir James Dewar for the kind advice he has given me.

Address of the President, Sir Archibald Geikie, K.C.B., at the Anniversary Meeting on December 1, 1913.

On these annual occasions it is usual to begin the retrospect of the year by discharging the melancholy duty of taking note of the losses which death has inflicted on our Society since the last Anniversary. On the present occasion we are fortunate in not having to deplore the passing away of any of the distinguished men who form the remarkable band of our Foreign Members. But on the other hand, the blanks which have been made in our Home List are exceptionally heavy, for no fewer than twenty of our Fellows have died, and among these some whose places it will for many years be hard to fill.

Especially numerous and serious have been the losses among those who represent the various departments of the Physical Sciences. In GEORGE HOWARD DARWIN we mourn the departure of one of the most brilliant and most estimable of our colleagues, who by the originality and distinction of his researches amply sustained the scientific renown of our publications and enhanced the prestige of the Society. He was elected a Fellow in 1879, served repeatedly on the Council, and was Vice-President during the last year of his presence there. He was awarded a Royal Medal in 1884, and only two years ago received as the crowning mark of our appreciation of his achievements in science the award of the Copley Medal. There was a widespread hope among the Fellows that he would this year be elected to the Presidential Chair of the Royal Society. But, while still with the promise of further years of fruitful work before him, he was attacked by a fatal disease which carried him off on December 7 last in the 68th year of his age. With admiration and pride we recall the keen insight and the laborious but brilliant calculations which culminated in the production of GEORGE DARWIN'S memorable essays on the history of our planet and its satellite. We remember the long years during which he devoted his mind to the study of the Tides, thereby elucidating that complicated subject, and at the same time rendering valuable service to the art of navigation. We think, too, of the many hours which, first and last, he cheerfully gave up to the furtherance of scientific progress by attendance on committees, boards, and congresses, not in this country only but also abroad, as representative of the Royal Society in international organisations. On this Anniversary, however, our thoughts turn more tenderly to the man himself as he lived and moved among us. Long shall we cherish the remembrance of the example of his gentle and studious nature, his unfailing courtesy and kindly cheerfulness, his ardour in the cause of scientific research, his large-minded tolerance towards those who differed from him, and that helpful sympathy, inherited from his illustrious father, which led him to take interest in each fresh advance of knowledge in every department of Nature, even in those furthest removed from his own special studies.

The late EARL OF CRAWFORD was a characteristic example of a type of men whereof the Royal Society, from the very commencement of its history, has continued to include instances—men of distinction in public affairs, who are keenly interested in scientific enquiries, who promote their progress, and who occasionally themselves contribute original observations of their own on subjects which they have personally studied. As the premier Earl of Scotland, with large estates to administer and taking an active part in public life, LORD CRAWFORD yet found time for the cultivation of research. In his youth he took to astronomy, and, with his father, built and equipped an observatory on his property in Aberdeenshire. Soon after coming of age he went to Spain, for the purpose of observing the solar eclipse of 1870, and four years later took a journey to Mauritius to observe the transit of Venus. These and other proofs of his scientific predilections contributed to his being elected into the Royal Society in 1878, when he was 31 years of age, and he had the unusual distinction of being chosen to serve on the Council in the same year. A further mark of appreciation was shown to him by his fellow-astronomers, who elected him President of the Astronomical Society. In later years he turned to the biological side of science, and as a yachtsman, sailing over the seas of the New as well as of the Old World, he was able to add a number of new species to the known bird-fauna of the globe. LORD CRAWFORD was likewise a lover of literature and the possessor of a noble library. He was thus well qualified to be a Trustee of the British Museum, an office to which he was elected in 1885. Up almost to the close of his life he was sedulous in his attendance at the meetings of the Trustees, showing always a keen interest in the organisation and administration of the two great national establishments at Bloomsbury and South Kensington.

Major-General HENRY CLERK, R.A., who died at the great age of 92, was the oldest surviving Fellow of the Royal Society, his election having taken place as far back as 1848. He was the author of papers on meteorological and other physical subjects, the earliest of which was printed in the 'Philosophical Transactions' for 1846.

The ranks of the physicists and teachers of physics in this country have been deprived by death of the Professor of Natural Philosophy in the University of Edinburgh—JAMES GORDON MACGREGOR. Born in Nova Scotia in 1852, he received his scientific training in this country and in Leipzig. After having held several educational appointments in his native colony, he was chosen in 1901 to succeed Peter Guthrie Tait in the important Chair of Natural Philosophy in Edinburgh. The value of his investigations in electrolytic conductivity and other properties of solutions, in the resistance of metals, and in thermo-electricity, led to his election into the Royal Society in the year 1900.

One of our most prominent losses this year has been the death of Dr. JOHN MILNE, the great pioneer of modern Seismology. Born in 1850 and trained at the Royal School of Mines, he at the age of 25 accepted an academic appointment under the Japanese Government as geologist and mining engineer, and for some twenty years resided in Japan. His attention was soon arrested by the abundant display of earthquake phenomena in that country, and he devoted himself with the greatest ardour to their investigation. He devised a delicate instrument whereby the complicated seismic movements could be accurately observed and recorded. His enthusiasm in the study communicated itself to the Japanese. With their co-operation he was enabled to establish a seismic survey of the country, embracing not far short of 1000 observing stations. He founded the Seismological Society of Japan, and in the voluminous Transactions of this Society, mostly the work of his own indefatigable pen, he gathered together the observations and deductions which served to give seismology its due place among the exact sciences of the earth. When he returned to this country in 1895, in order to make here his permanent home, his first care was to find some site where a seismological observatory could most effectively be placed, and he finally selected Shide, in the Isle of Wight, which henceforth became famous as the centre of the great network of observing stations which, with the co-operation of the British Association for the Advancement of Science, he proceeded to institute not only in this country and our dependencies, but even over a large part of the rest of the globe. The records transmitted to him from this world-wide organisation were discussed in annual reports to the British Association, and in course of years he had the gratification of seeing his example followed in other lands. Japan, fostered by his enthusiasm, had led the way. Various countries in Europe undertook the recording of earthquakes likewise, until eventually an International Seismic Association was formed for concerted observation and experiment in regard to seismological problems. Had he lived and retained his health, it was the hope of his friends that MILNE might be prevailed upon to accept the control of such an international organisation and bring into its operation the world-wide system of stations which he had established with so much skill and labour and had supervised with such signal success. But his vigour had been for some time past perceptibly lessening. After a brief illness he died on July 30 last, at the age of no more than 62. His career presents a memorable example of what can be accomplished in the cause of science by clear-sighted intelligence and indomitable application. His admirable organisation of observing stations, though now bereft of his guidance, must not be allowed to lapse or suffer any serious interruption. Provision has meanwhile been made for continuing the work as he left it. The Royal Society and the British Association for the Advancement of Science have each formed a committee which will co-operate in considering what further steps should be taken. It would be little to the credit of the scientific reputation or public spirit of this country if means could not be found to place MILNE'S organisation in a position of permanent security and usefulness. It is an institution actually at work, it is capable of expansion and improvement, and it is eminently worthy to be the basis or nucleus of an imperial, if not international, enterprise, prosecuting work advantageous to the whole world.

The representation of Chemistry on the list of Fellows of the Society has been diminished during the past year by the death of Sir WALTER NOEL HARTLEY, who was for so many years one of the leaders of science in Dublin, where he held the Chemical Professorship at the Royal College of Science. His spectroscopic researches were especially notable and received well-deserved recognition. He was elected into the Royal Society in 1884. He died on September 11 last, in his 68th year.

Dr. HUGH MARSHALL early attracted attention by his researches in chemistry, mineralogy, and crystallography. While still a young man, he was in 1904 elected into the Royal Society, and four years later he received the appointment of Professor of Chemistry in University College, Dundee. But his brilliant promise was cut short by his death on September 6 last, at the early age of 45.

By the sudden death of Sir **William White**, on February 27, in the 68th year of his age, we have lost one of our foremost Fellows in engineering science. His long experience at the Admiralty, culminating in his appointment to be Director of Naval Construction, gave him a position of commanding authority in all that appertained to the science of naval architecture, to which he contributed valuable memoirs and treatises. But he had many interests outside his own profession. Possessing a remarkable capacity for affairs and a faculty of clear exposition of his views, he came to be chosen a member of innumerable committees, boards, and other deliberative bodies, wherein his long experience and ripe judgment were much appreciated. In his later years he was more especially interested in the progress of education in applied science. He was one of the most active members of the governing body by which the Imperial College of Science and Technology was organised. He likewise served on the Committee to which the consideration of the constitution of the new Science Museum was referred by the Government. He became a Fellow of our Society in 1888, and six years thereafter he served for a year on the Council.

Another loss to the engineering section of the Royal Society has been inflicted by the recent death of Sir **William Preece**, who will long be remembered for his valuable services in the development of the practical applications of electricity. As head of the Telegraphic Department of the Post Office for more than twenty years he had ample opportunity of applying his scientific experience to the expansion of this important branch of the public service. For example, he took a keen interest in the applications of the telephone from the time when he introduced Mr. Graham Bell's invention into this country. He took an active share in the early experiments which led to the establishment of telephonic communication with the continent of Europe. He was in this country a pioneer in the practical adoption of wireless telegraphy. He was born in 1834. His election into the Royal Society took place in 1881, and six years thereafter he served for two years on the Council.

Mr. **George Matthey**, who died on February 14 at the advanced age of 88, represented the aims of metallurgy in our list of Fellows. His extensive researches on platinum led to his being consulted many years ago by the French Government regarding the material to be employed for the construction of the standard metre and this standard was ultimately manufactured of iridio-platinum by his firm under his own supervision. He became a Fellow of the Society in 1879.

Only last week another gap was made among the physicists of the Royal Society by the death of Sir **Robert Ball**, in the 74th year of his age. Distinguished as a mathematician, experimentalist, and physicist, he began by making important discoveries of nebulæ with the great Rosse telescope. Thereafter his remarkable paper "On the Theory of Screws" was published in the 'Transactions of the Royal Irish Academy' in 1872. He was elected into this Society in the following year. From 1874 onwards he specially devoted his attention to astronomy, becoming Professor of that science at the University of Dublin and Astronomer Royal for Ireland. In 1892 he was appointed Lowndean Professor of Astronomy and Director of the Observatory at Cambridge. His contributions to astronomical science included many investigations to determine the distances of a large number of fixed stars from observations of their annual parallax. When he undertook the part of an expositor of science to popular audiences he soon acquired a wide reputation both as a lecturer and a writer of readable and interesting books. His astronomical volumes, which attained a wide circulation, were important means of disseminating an appreciation of the fascination of the science to which he was devoted. Sir ROBERT BALL will be sincerely mourned by all who were privileged with his friendship, and by that still wider circle who knew him less intimately but came under the spell of his kindly and humorous talk and the sparkle of his genuine wit.

On the Biological side of science our losses this year, though less numerous than those on the physical side, are notably serious on account of the eminence of the Fellows who have passed away. Foremost among them we have to record that within the last few weeks ALFRED RUSSEL WALLACE has gone to his rest, ripe in years and full of honours, amidst the unstinted appreciation not only of his own countrymen, but of every civilised people. A true naturalist, in the old and fullest sense of the term, every living thing was interesting to him not only in itself, but more especially in its relations to other organisms and to the distribution of life over the globe. At the early age of 25 he began his scientific career as an explorer and collector in tropical regions, first in South America and afterwards in the Malay Peninsula. For the long period of sixty-five years, almost up to the close, he has continued with unfailing vigour to prosecute the studies to which he dedicated his life, continually publishing fresh contributions to natural history and to the consideration of social problems. His 'Travels on the Amazon and Rio Negro,' 'Malay Archipelago,' 'Geographical Distribution of Animals,' and 'Island Life' have become classics in zoological literature. In his writings there is everywhere proof of the remarkable range of his knowledge, the closeness and accuracy of his faculty of observation, and the breadth of view wherewith he co-ordinated his facts and drew from them wide and suggestive generalisations. As is well known, it was in the Malay Archipelago, amidst the marvellous variety and exuberance of tropical life that, with the divination of true genius, he evolved the same theory of the origin of species on which Charles Darwin had already been at work for some sixteen years. Some of us well remember the sensational meeting of the Linnean Society in the summer of 1858 when papers from the two naturalists, who had independently arrived at similar conclusions, were communicated by Sir Joseph Hooker and Sir Charles Lyell. No incident in the history of modern science is more worthy to be recalled than the chivalry with which the work of the young and little known explorer, pondering over the problems of evolution amid the solitudes of a tropical forest, was received and placed at once side by side with that of the brilliant naturalist whose fame had already spread over the world, and at the same time the generous solicitude on Darwin's part that full justice should be done to his younger competitor. Their names will live for all time as those of the great Twin Brethren to whom science owes the first intelligible exposition and elucidation of the problem of the origin of species. WALLACE was connected with the Royal Society by a number of links, each of which marks the Society's recognition of the importance of his contributions to natural knowledge. As far back as the year 1868 he received one of our Royal Medals. In 1890 he was appropriately selected as the first recipient of the Medal which had recently been instituted in honour of Charles Darwin. In 1893 he was elected with acclamation a Fellow of the Society, and in 1908 the highest honour which it is in our power to bestow, the Copley Medal, was conferred upon him. Born in 1823, he died on November 7 in the 91st year of his age.

The death of ADAM SEDGWICK has removed from our midst one of the most brilliant zoologists of his day. We look back upon his notable career at Cambridge as an original investigator and stimulating teacher, where he remodelled the zoological school, making it a great centre of biological training and research, and filling it with ardent pupils, who caught his enthusiasm, and bore it with them into other seats of learning. It seems only yesterday, although some six years have meanwhile slipped away, since with some hesitation he brought that Cambridge life to a close and accepted the Professorship of Zoology in the Imperial College of Science and Technology. There a fresh career of fertile teaching and practical research in biology and embryology seemed to open before him. Coming with a great reputation to fill the chair formerly made famous by Huxley, he at once threw himself with his wonted energy into the task of restoring the efficiency of his department, which had somewhat suffered from the prolonged want of a successor to the previous professor. It was fondly believed that his biological school in London would soon equal, or even surpass, in success his school at Cambridge. But after two or three years his health was seen to begin to give way. He died on February 27 last at the age of 55. He became a Fellow of the Royal Society in 1886, and served twice for two years on the Council.

LORD AVEBURY belonged to a class which is becoming less numerously represented in the Royal Society than it used to be—the class of the cultivated country gentleman possessed of leisure and means, and devoting these to the cultivation of scientific studies. He was a man of singular versatility. Inheriting an estate in the country, where he spent much of his time, he was antiquary, archæologist, botanist, zoologist, geologist, also Member of Parliament, chairman of many various mercantile associations, councillor, if not president, of most of the chief scientific societies of this country, and all the while head of one of the great banking firms of London, and actively engaged in its concerns. In the City he was looked up to with universal respect as one of the leading authorities on mercantile affairs. Elsewhere he was known chiefly as a man of science, while thousands of readers throughout English-speaking countries were familiar with his contributions to popular literature. In the midst of a life which flowed on with so ample a current, he found time to write some noteworthy treatises. His volumes on 'Prehistoric Times' and 'The Origin of Civilisation and the Primitive Condition of Man' were of no small service in the infancy of the study of archæology. His contributions to entomology and to botany showed how much natural history might have benefited had he been able to devote his whole time and energy to original observation. And apart from his own writings, LORD AVEBURY was able in many ways to advance the cause of science. In his capacity of member of the Standing Committee of the Trustees of the British Museum, an office to which he was appointed as far back as 1878, he was unremitting in his zeal for the interests of that great national institution. His presence on the Councils of scientific societies was always helpful. He became a Fellow of the Royal Society in 1858, when he was only 24 years of age, and he served altogether seven years on our Council, and was three times Vice-President. LORD AVEBURY was a notable social force. Eminently hospitable, he brought the cultivators of science into touch with men in other walks of life. At High Elms, his country home in Kent, or at Kingsgate Castle, on the edge of the chalk cliffs, he loved to gather together men of culture in all branches of human activity, and from all parts of the globe. Again, at his house in London, he kept up the now well-nigh obsolete custom of giving breakfasts, which were pleasant reunions and by no means the least efficient of the ways he followed to make men acquainted with each other. He leaves behind him a social blank which will be felt not less than the absence of his wise counsel at the many boards and committees of which he was a member.

Mr. PHILIP LUTLEY SCLATER, who died at the age of 84, was a conspicuous example of a country gentleman who can take up a branch of science as the main occupation of his life and make himself one of its recognised leaders. During his student years at Oxford he was induced to interest himself in ornithology, which eventually became his engrossing pursuit. Able to travel extensively, both in the Old and the New World, he always kept his eye on the birds of the regions through which he passed, thus acquiring an extensive acquaintance with systematic ornithology. This knowledge served him in good stead in his well-known discussion of the geographical distribution of animals and his remarkable classifica- of the zoological provinces into which the surface of the globe may be divided. He will long be remembered for his lengthened and intimate association with the Zoological Society. For upwards of forty years he continued to be annually elected its Secretary, devoting himself with unwearied diligence to the furtherance of its interests, of which he came to be regarded as the visible incarnation. He was a Fellow of the Royal Society for more than half a century, having been elected in 1861. He served twice on the Council.

In Prof. FRANCIS GOTCH physiology has lost one of its brightest ornaments. Alike as an original investigator of the physiology of the nervous system and as a luminous and stimulating expositor of the subject, he has conferred lustre on the Oxford physiological school. He was elected into the Royal Society in 1892, and served for two years on the Council. He died on July 17 last, aged 60.

Sir JONATHAN HUTCHINSON, famous as one of the great surgeons of his day, eminent for his original contributions to medicine, untiring in his zeal for the promotion of the study of natural history, and conspicuously generous in his establishment and support of country museums to give that study an educational value, passed away last summer at the ripe age of 85, amidst the sincere sorrow of all who came into intimate touch with him. He was elected into the Royal Society in 1882, in recognition of the importance of his papers on the natural and clinical history of disease in man and the lower animals.

It was with much regret that we heard that EDWARD NETTLESHIP passed away on the 30th October last. Pre-eminent as an ophthalmic surgeon he enriched his department of clinical medicine with many admirable papers descriptive of his observations. When he retired from a large practice in London to the quiet of a country home he devoted his time and enthusiasm to the study of heredity and obtained results of great interest. Elected into the Royal Society only last year, he took a part in the work of the Committee for the investigation of glassworkers' cataract. His retiring disposition was apt to conceal from those who only knew him casually the enthusiasm and originality with which he pursued the study of nature; his gentle, lovable, and generous character could only be fully appreciated by those who knew him best.

In the Report presented by the Council the more important events in the history of the Society during the past year are recounted. Among them I would here make special reference to the magnetic re-survey of this country. It has been arranged that the operations of this survey will include the 200 stations of the original survey by Sir Arthur Rucker and Sir Edward Thorpe, together with forty additional stations along the line of the Yorkshire ridge. Mr. G. W. Walker, to whom the work has been entrusted, informs me that he began in August last the preliminary task of gathering together the requisite instruments and apparatus. The needful maps were supplied by the Ordnance Survey Department; the Admiralty furnished chronometers; the Astronomer Royal has been good enough to undertake to afford control observations from Greenwich, and Prof. Newall has kindly given the use of a large field adjoining the Cambridge Observatory to serve as a base station. The apparatus belonging to the Royal Society, which had for some years been lent to the Falmouth Observatory, has now been placed at Mr. Walker's disposal. The first observations were started at Cambridge on November 10, and these will be continued concurrently with the standardisation of the apparatus. The Eastern Counties will forthwith be attacked during the coming winter, although that part of the year is least favourable for work of this nature. It is believed that the re-survey will be completed within less than two years.

There is another paragraph in the Council's Report to which I may here allude. Five years ago at the request of the Home Office the Council appointed a Committee to investigate the physical and physiological problems presented by the disease known as Glassworkers' Cataract. In proposing this enquiry the Home Office had made no provision for the cost of the numerous experiments and examinations that obviously would be required, while the Royal Society has no funds at its disposal for meeting such expenditure. As only a small sum has been contributed by the Treasury the work of the Committee has been seriously delayed. Only one branch of the investigation has been practically completed—the branch undertaken by Sir William Crookes—and this could not have been accomplished had he not borne a large part of the heavy cost at his own charges. He set himself to discover whether a glass could be devised that would screen the eyes of the glassworkers from the heat and glare of the molten material with which they have to deal. After an extensive and complex series of experiments he has been able to prepare glasses which cut off more than 90 per cent. of the heat radiation, which are opaque to the invisible ultra-violet rays, and are sufficiently free from colour to be capable of use as spectacles. It has not been possible, for lack of funds, to proceed far in the investigation of the physiological problems involved in the study of Glassworkers' Cataract; the Committee is consequently still unable to present a complete Report.

In the Address which I gave at the end of the first year of my tenure of the office of President I dwelt at some length on the varied activities of the Royal Society, and alluded to the imperfect extent to which these are known to the world outside. Speaking now at the close of my Presidency I would like once more to refer to this subject, and in connection with it, to the position which the Society holds in relation to the State. I would again point out that ours is not merely a Society which holds meetings for the reading and discussion of scientific papers, publishes these communications in its 'Proceedings' and 'Transactions' and acts generally for the promotion of the progress of science. Our meetings and our publications are undoubtedly a highly important part of our work, but they by no means comprise the whole field of our operations. The Royal Society is the one great institution in this country which selects its component members from among the most distinguished men in each of the various branches of pure and applied science. It has thus acquired the character of a kind of central Council of Science, and may legitimately claim that few scientific problems could arise affecting modern life for the solution of which the most extensive experience and the most authoritative opinion would not probably be found within its own representative ranks. While this comprehensive capacity for practical usefulness has from the beginning distinguished the Society, it has only in comparatively recent years been to any considerable extent recognised by the State. The various Departments of Government have slowly realised that the Society includes a large body of trained specialists who are able and willing to give their time and thought to the service of the country in matters where scientific experience is needful. The public recognition of this ready serviceableness has greatly increased the range of the Society's activities. The various enquiries into the nature and prophylaxis of tropical and other diseases which, at the request of different Departments of the Government, the Society has undertaken in recent years and is still carrying on, may be cited as examples of the nature of the services which we can render in biological matters of Imperial concern. Again, the fostering care with which the Society has watched over the rise and progress of the National Physical Laboratory, likewise the participation which it has been asked to take in international associations for geodetic, seismological and other investigations, shows that on the physical side of science its operations have been not less continuous and beneficent.

It would be impossible that these various lines of enquiry should be adequately pursued were not the labour distributed over a number of boards and committees composed of members selected by the Council for their eminence in the branches of science which they severally represent. The leaders so chosen are often busy professional men, yet they cheerfully give their time and experience to the consideration of the questions submitted to them, and come, even from long distances and entirely at their own charges, to the meetings and conferences in Burlington House. It is, needless to say, a source of great satisfaction to the Royal Society that its services should now in this manner be made use of for the benefit of the country and of humanity at large.

There is unfortunately, however, a prevailing but mistaken impression that a society which can thus freely place its knowledge and experience at the disposal of the State must be a wealthy body. It is true that we administer every year a considerable sum of money; but almost the whole of this sum is ear-marked for certain definite objects and cannot be diverted to anything else. Even the annual Parliamentary grant of £4000 for scientific investigation, which is placed in the hands of the Society, is not a contribution to the Society's own operations. The whole of it, except the trifling sum required for clerical assistance and necessary printing, is allocated to applicants from all parts of the country for their individual researches. Fellows of the Royal Society may indeed enter into the list of applicants, but the number of those who do so does not amount to one-fourth of the whole. The Society, by means of its various committees and boards, expends much time and care in sifting and considering the applications, but it employs no part of the grant in the furtherance of its own corporate aims. There is a second annual Parliamentary grant of £1000 made to the Royal Society to assist in defraying the expenses of publication. But it is understood that a portion of this sum is to be set aside for the purpose of aiding the adequate publication of scientific matter through other channels and in other ways. Thus the whole of the subvention which the Society receives annually from the State for its own requirements amounts to only a few hundred pounds towards the cost of its publications, together with the use of its rooms in Burlington

House, where it sits rent free, but subject to expenditure for internal upkeep and repairs.

From time to time valuable benefactions have been made to the Royal Society by some of its Fellows and also by generous donors outside its pale. Without this help it would have been impossible to undertake much of what we have accomplished, and the usefulness of the Society would have been greatly restricted. It is to the continuance of such generous donations in the future that we may most hopefully look for the means of strengthening the position and increasing the usefulness of the Society. But the legacies and donations hitherto made to us have for the most part been assigned for certain specific ends, and cannot be devoted to other purposes which from time to time the Society would be glad if it could undertake. Some years ago the President and Council took this question of benefactions into their serious consideration, and issued a notification, which appears in every number of the Year Book, to the effect that, while they will willingly receive gifts to be applied to special objects or for the benefit of particular sciences and would wish, wherever desirable, to associate the name of the benefactor in some conspicuous manner with his gift, they consider that, in view of the varying necessities of Science, the most useful benefactions are those which are given to the Society in general terms for the advancement of Natural Knowledge.

As so much of the funds in possession of the Royal Society is applicable only to certain definite purposes, the balance available from the yearly income, after all expenses have been defrayed, is never large, while occasionally it is actually replaced by a deficit. In these circumstances it has been difficult for the Society to carry on and complete some of the enterprises which, in the general interest of science, it has undertaken. Thus, but for the generous assistance of the late Dr. Ludwig Mond, it would have been impossible to prepare the voluminous Catalogue of Scientific Papers for the Nineteenth Century, without seriously trenching upon the funded capital of the Society. But the donation of that liberal member of our body is now nearly exhausted, and we have to face an expenditure of at least £5,000 before this important work can be completed and published. Again, the rapidly growing expansion of the National Physical Laboratory, while it is a matter of which the Royal Society has good reason to be proud, is at the same time one which cannot be contemplated without a little misgiving. The Society is financially responsible for the Laboratory, which now has an annual expenditure of £30,000. So long as the receipts exceed that sum we incur no loss, though we have to guarantee an overdraft at the bank to the amount of £3500. But should any serious falling off of the receipts arise, such as would be caused by depression in trade or strikes or other causes of the interruption and stagnation of industries, there might be a heavy deficit, for it would not be possible to reduce at once the working expenses of the institution. Obviously the Society, through the success and growth of the Laboratory, has been placed in a position like that of a manufacturer who tries to carry on an extensive business with a reserve balance of only a few hundred pounds. This is a position which it is not desirable that we should hold, and from which we ought to be relieved as speedily as possible.

When we consider the amount and value of the gratuitous service given at the request of the various public Departments, it is abundantly obvious that the Government of this country is under special obligations to the Royal Society, which, were they expressed in the plain language of professional practice, would be indicated by a considerable sum of money. We have assuredly no desire that this service should cease to be gratuitous. We are at all times ready, as far as lies in our power, to place our time, our knowledge, and our experience, without stint, at the service of the country. But it is well that in the financial dealings of the Government with the Society, and in the due care for economies, which is a paramount obligation of all Governments, the commercial value of this unpaid labour should not be lost sight of. We claim that our disinterested action deserves to be recognised by at least a generous and sympathetic attitude on the part of the Government towards our aims and objects, and a disposition to help us when our means prove inadequate to carry out the work which we have undertaken for the furtherance of the progress of science.

Since this Address was written I have within the last few days received a donation which I have the pleasure of now announcing. Sir James Caird, Bart., of Dundee, so well known for his munificent benefactions to science, has sent me a cheque for £5000 to be expended in yearly disbursements of about £500 for the furtherance of Physical Research. We are grateful to him for this generous and timely gift, which can be at once applied to the furtherance of investigations in which we are now engaged and for which our present available funds are inadequate. It appears to me that the Royal Society will never be sufficiently provided for that active support of research which its position demands until it is in possession of an annual sum of at least £1000, apart from its ordinary income, which it can devote to any investigations that call for pecuniary assistance. It often happens that subjects arise regarding which it is highly desirable that enquiry should be undertaken, but where serious expense is involved the Society finds itself crippled for want of funds. I am not without hope that among our wealthy Fellows and among the still richer men in the community outside, some may be led to perceive that by donations or bequests to the Royal Society they will contribute to the accumulation of such a reserve as I have indicated, which will enable the Society to further the advance of Natural Knowledge in a manner more effective than it has ever yet been able to attain.

MEDALS.

The Copley Medal is this year assigned to Sir Edwin Ray Lankester, in recognition of the value of his original researches in Zoology and of the importance of his personal influence in stimulating the investigations of his pupils and others, which have materially extended the boundaries of our knowledge of the Animal Kingdom. His own work, which has been in large measure morphological, has thrown light on the mutual relations of living animals and also on the structure and affinities of long extinct organisms. His researches in the comparative embryology of the higher Mollusca and of the anatomy of the Nautilus gave him an assured place among the zoologists of his day. His early papers on the Ostracoderm Fishes of the Old Red Sandstone afforded a memorable example of palæontological acumen. In addition to his original investigations, he has laid Zoology under a debt of gratitude to him for his luminous general articles in some of the larger departments of the science. His pupils speak with enthusiasm of his inspiring guidance as a teacher, and some of the outstanding results of their labour confessedly owe to him the impetus that carried them to a successful issue. In later years Sir Edwin, though retired from official life, has continued to be unceasingly active in the cause of Natural Knowledge. Ensconced in his "Easy Chair," he discourses pleasantly to a large audience in the outside world, while from time to time he enlivens the dullness of life with letters to the Press, written with that caustic pen which he knows so well how to wield.

The Council's awards of the two Royal Medals annually presented by the King have received His Majesty's approval. The Medal on the physical side has been adjudged to Prof. Harold Baily Dixon, to mark the Society's appreciation of the importance of his long continued investigations of the phenomena of gaseous explosion. His important observations on the Theory of Combustion have shown that water-vapour acts as a carrier of oxygen during the oxidation of carbon, and undergoes a cycle of changes wherein it gives up its oxygen to carbon monoxide. From the further study of the explosion of this monoxide and oxygen, in the presence of other gases, he concluded that any substance capable of producing steam will determine the explosion. Reference may be made to his published papers on the explosion, oxidation, and combustion of various substances, together with his numerous determinations of the specific heat of gases at high temperatures. We recall also his Bakerian Lecture on the Explosion of Gases, which was given in this room twenty years ago. By the introduction of photography into his studies of the explosive wave he has been able to throw light on the mode of burning of carbon and its compounds. Recognised as a brilliant investigator of Explosion and Combustion, he was fitly selected to be a member of the Royal Commission on Explosions in Mines, and he is taking an important part in connection with the experiments on explosions of coal-dust, now being carried on at the instance of the Government.

The Royal Medal on the biological side is bestowed on Prof. Ernest Henry Starling as a mark of the Society's high appreciation of the wide range of his contributions to the advancement of physiology. By his enquiry into the relation of lymph production, and the absorption of fluids from the peritoneal cavity and the cavity of the eye-ball, he showed the dependence of these processes upon the osmotic pressure of the blood and tissue fluids and the hydrostatic pressure in the blood vessels. He traced the connection between the glomerular activity of the kidney and the osmotic pressure of the serum proteins. In the course of this investigation he measured the osmotic pressure of the serum proteins by an improved method. In his excellent studies of the mammalian heart he has greatly improved the technique. By much reducing the volume of blood needed to maintain a circulation through heart and lung, he has increased the sensibility of the preparation to variations of state, and by introducing into the circuit of the blood a readily adjusted resistance to the flow he can ascertain the effects of the obstacle upon the heart's action. He has thus been able to show that the rate of beat depends solely upon temperature, and varies directly with temperature; and that the output is independent of resistance and temperature, but varies directly with the venous inflow up to a certain limit beyond which congestion of the lungs occurs. He has discovered that the normal heart of the dog will consume 4 mgrm. of sugar per gramme muscle per hour, but that if the animal is diabetic, the heart is incapable of consuming sugar—an observation of singular value in the light it throws upon the cause of diabetes. But besides the original contributions made by Prof. Starling alone or in conjunction with his pupils, we must bear in mind the brilliant and fundamental work which he accomplished in association with Dr. Bayliss. To the latter Fellow of the Society a Royal Medal was awarded two years ago, and it is only fitting that his friend and co-worker should now receive a similar honour.

The Davy Medal has been awarded to Prof. Raphael Meldola, in acknowledgment of the distinction of his contributions to synthetical Organic Chemistry, especially in the series of aromatic compounds. He discovered the first representative of the oxazines, a group which has since been developed into one of great importance. He has contributed to the chemistry of naphthalene derivatives, and carried out extensive researches upon the azo- and diazo-compounds, with results which have an important bearing upon the question of the constitution of these compounds. He has likewise added to our knowledge of the chemistry of other groups of nitrogen-containing compounds, notably the triazines and the iminazoles. Of late years he has shown the synthetical value of compounds containing a mobile nitro-group, and has discovered a remarkable new class of quinone-ammonium derivatives. He is the author of several well known treatises on chemical subjects; among the latest of these, one entitled 'The Chemical Synthesis of Vital Products,' has taken rank as a standard work of reference in the important field of which it treats.

The Sylvester Medal is conferred this year on the veteran mathematician, James Whitbread Lee Glaisher. His prominent career in mathematical science, which began at an early age, has been continued down to the present day without remission, not only in the production of original papers, but in University teaching, and in the careful editorship of most of the special mathematical journals in this country. To these journals he has constantly contributed much of his own work, such as his papers on the Theory of Numbers, on Elliptic Functions, and many other departments of pure mathematics. We desire to recognise his single-minded devotion to the science to which he has dedicated his life. We trust that the award of this Medal will be acceptable to him, as once more associating his name with that of his old friend, Sylvester, with whom he was so closely bound in editorial and other labours.

In considering the bestowal of the Medals this year the Council has determined to award the Hughes Medal to one who has spent his days in the application of scientific discovery to practical life—Alexander Graham Bell. Although he has been resident for many years on the other side of the Atlantic Ocean, we remember that he was born in Edinburgh, and was educated there and in London, so that we claim him as a fellow countryman. His preponderating share in the invention of the telephone, now so long ago as 1876, and his practical investigations in phonetics, have laid modern civilisation under deep obligation to him, while his numerous other inventions and experiments show the fertility of his genius. The Hughes Medal appeared to the Council to be the most appropriate mark of our appreciation which could be offered to a man whom we specially desire to honour.

One final duty remains for me to perform before I retire from this Chair. I have to thank the Fellows of the Society for the great honour which they conferred upon me when they elected me to be their President, and also for the kindness and sympathy with which they have surrounded me during my tenure of the office. To the Council, the Officers, and the permanent Staff I would express my grateful appreciation of the uniform helpfulness and cordiality with which they have assisted me in the discharge of the multiform duties that appertain to the Presidency. These last five years have been to me a singularly full and happy time, the memory of which will ever be to me a delightful retrospect. It is my belief that I leave the affairs of this great Society in a not less prosperous condition than that in which they were entrusted to me. I shall hand over the reins of Office to one whose scientific achievements confer a lustre on the Royal Society, and whose long experience of the conduct of our work gives the best assurance that the prosperity of the Society in past years will be amply maintained in those that are to come.

The Analysis of Crystals by the X-ray Spectrometer.

By W. Lawrence Bragg, B.A.

(Communicated by Prof. W. H. Bragg, F.R.S. Received November 13,—Read November 27, 1913.)

In a former communication to the Royal Society,[*] an attempt was made to determine for certain crystals the exact nature of the diffracting system which produces the Laue X-ray diffraction photographs. The crystals chosen for particular investigation were the isomorphous alkaline halides NaCl, KCl, KBr, and KI. As in the original experiments of Laue and his collaborators, a thin section of crystal was placed in the path of a narrow beam of X-rays, and the radiation diffracted by the crystal made its impression on a photographic plate. By noticing what differences were caused in the photograph by the substitution of heavier for lighter atoms in the crystal, a definite arrangement was decided on as that of the diffracting points of the crystalline grating.

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[*] W. L. Bragg, 'Roy. Soc. Proc.,' A, vol. 89, p. 249.

Though it was found possible in the case of these simple salts to determine the position of the atoms of alkaline metal and halogen, which constitute the elements of the dimensional diffraction grating, yet this method, which may be called the photographic method, is very limited in its range of applications. It was only the extremely simple nature of the NaCl structure which made its analysis possible. On the other hand, the X-ray spectrometer, which has been devised by W. H. Bragg for the purpose of studying the reflection of X-rays by crystals,* affords a very much more powerful method of research into the structure of the crystal.

The photographic method works by throwing on the crystal a beam of "white" X-radiation, and comparing the strength of the beams reflected by various types of planes (nets) of the point system on which the atoms are arranged. The X-ray spectrometer employs a monochromatic radiation and faces are examined in detail one by one. In the first place, the spectrometer tells the distance in centimetres of plane from plane parallel to these faces. Moreover, if the successive planes are of identical composition, the results of the examination show this. If on the other hand the planes occur in groups, each group containing several planes of different nature, it is hoped that the results given below will show how the instrument can be made to give the exact spacing and relative masses of the planes of these groups. This means that we can obtain enough equations to solve the structure of any crystal, however complicated, although the solution is not always easy to find. In this paper I wish to indicate the solution for several types of crystals. For many of the experimental results I am indebted to my father, the rest have been obtained in Leeds with one of the spectrometers which he has constructed.

Parallel to any one of its possible faces, a crystal may be regarded as being built up of a series of planes. Each plane passes through the centres of one or more sets of atoms identical in all respects. The successive planes, encountered in proceeding in a direction perpendicular to the face under consideration, may not be identical in their character. They can always, however, be divided into groups in such a way that each group contains a sample of every kind of plane, arranged in an invariable order. It is proposed to call the distance between the groups $d_{(hkl)}$ when (hkl) are the indices of the crystal face. The pattern of the arrangement of planes repeats itself in the distance $d_{(hkl)}$.

As an example of the arrangement of these planes, we may take the cubic crystal of sodium chloride, NaCl. The structure of the crystal has been given in the paper cited above. It is there shown that the arrangement of sodium and chlorine atoms in this crystal must approximate closely to that given in fig. 1. Here we have points of two kinds, black and white, arranged at the corners of a set of cubes. Parallel to any cube edge such as AB, the points are arranged in rows of alternate blacks and whites. The measurements of the single crystal give only this arrangement of points of two kinds, and do not *ab initio* indicate how many atoms are to be associated with each of the points. For the sake of simplicity the assumption was made that each point represented a single atom. Every crystal investigated has strengthened the probability of the truth of this assumption, for it can be shown for the other crystals, whose structure has now been discovered, that if the points in fig. 1 represent a group of n atoms, the diffracting points of all these crystals also represent a group of n atoms. It seems very improbable that this should be true for such different crystals as the alkaline halides, ammonium chloride, diamond, fluor, the pyrites class, zinc blende, the calcite class and dolomite, for all of which the structure has been found. In view of this, it will be assumed that the diffracting points are atoms.

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* W. H. Bragg and W. L. Bragg, 'Roy. Soc. Proc.,' A, vol. 88, p. 428.

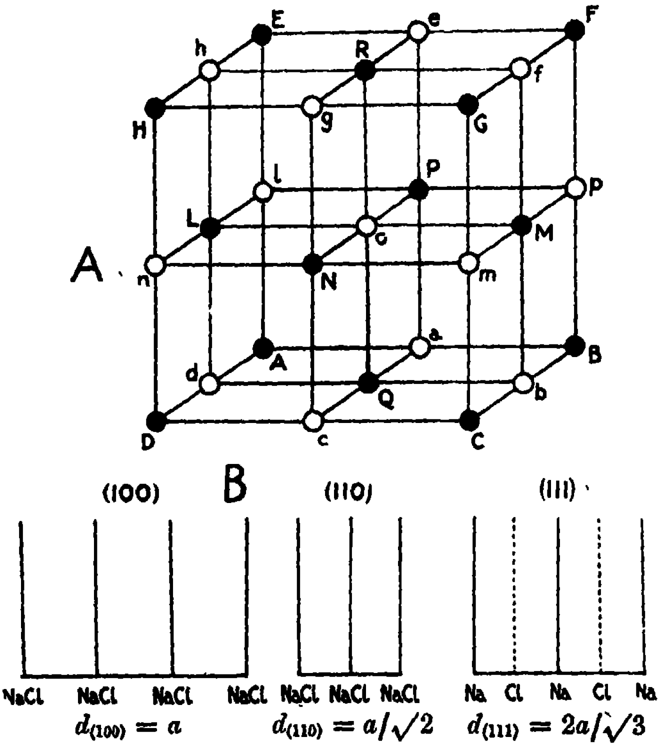

Fig. 1.

Planes parallel to the cube face ABCD contain both sodium and chlorine atoms in equal numbers. The successive planes ABCD, *lpmn*, EFGH, are identical in their properties, and if we take the side AD to be equal to $2a$, these planes are separated by a distance a. Thus we have $d_{(100)} = a$.

The planes parallel to DBFH also contain both sodium and chlorine atoms, and successive planes are identical. It is easy to see that $d_{(110)} = a/\sqrt{2}$.

It is different in the case of planes which are parallel to EDB, with the indices (111). The plane EDB passes through sodium atoms alone, as can be seen by consulting the figure. The next plane *efh* passes through chlorine alone, the next again through sodium alone. We have to proceed a distance equal to the perpendicular from E on AFH in order pass from one sodium plane to the next. Thus we have $d_{(111)} = 2a/\sqrt{3}$.

These results are represented in fig. 1 B.

We will now consider the evidence given by the X-ray spectrometer concerning the nature of these planes. When monochromatic radiation falls on a series of equally spaced planes, each of which can reflect only a small fraction of that radiation, reflection is practically non-existent unless the relation

$$n\lambda = 2d \sin \theta$$

holds good. λ is the wave-length of the incident radiation, θ the glancing angle of reflection, d the distance between the successive planes and n a whole number. Thus reflection is possible at a series of angles θ_1, θ_2, θ_3, etc., whose sines are in an arithmetical progression, got by substituting integers for n. The source of the monochromatic radiation used in these investigations was an X-ray bulb with anticathode of palladium. It has been shown by W. H. Bragg* that this metal gives off very little general radiation indeed, a large proportion of the energy in the spectrum being concentrated in two lines, one of which is much stronger than the other. It is this strong palladium line which is referred to below. Its wave-length is equal to $0{\cdot}576 \times 10^{-8}$ cm.

Examples of the curves obtained, when investigating the reflection from a crystal face, have been given in former papers. A series of measurements of the strength of the reflected beam for different angles are made, the crystal and ionisation chamber being always set so that the one reflects into the other. At all angles there is a general reflection. At the angles θ_1, θ_2, θ_3 which satisfy the condition

$$n\lambda = 2d \sin \theta,$$

when $\lambda = 0{\cdot}576 \times 10^{-8}$ cm., a strong special reflection is superimposed on the general. By subtracting the reflection at these angles from that at neighbouring angles, a measure of the intensity of this special reflection is obtained. The amount of general reflection is almost always small compared with the special reflection, when a palladium bulb is used.

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* *Supra*, p. 430.

In this paper the intensities of the spectra and the angles of reflection will alone be given. In some cases investigated by my father, the bulb used had a rhodium anticathode, rhodium having a spectrum almost identical with that of palladium.

Table I.

The angles give the setting of the ionisation chamber. The numbers are proportional to the intensities of the spectra.

Rock salt, Pd rays—										
(100)	100	11·7°	30	23·8°	7	36·2°				
(110)	100	16·5°	24	34·0°	7	52·0°				
(111)	20	10·2°	100	20·6°	0	—	6	42·5°		
Fluor spar, Pd rays—										
(100)	0	—	100	24·5°	0	—	18	50·5°		
(110)	100	17·4°	16	35·4°	6	51·5°				
(111)	100	10·7°	0	21·5°	10	32·5°	9	43·7°	3	53·5°
Zinc blende, Rh rays—										
(100)	40	12·8°	100	25·9°	0					
(110)	100	18·2°	25	37·2°	7	57·5°				
(111)	100	11·4°	5	23·0°	8	34·7°				
Pyrites, Rh rays—										
(100)	100	13·0°	0	26·2°	0	39·6°	14	53·8°	4	69·0°
(110)	100	18·1°	50	37·2°	0	—	0			
(110)	80	11·4°	100	22·6°	50	34·2°	0	—	22	58·8°

The intensities of the rock-salt spectra will be found in Table I. The results for the faces (100) and (110) are of what may be called the normal type. The reflection of the first order, for which θ[*] has the value given by

$$\lambda = 2d \sin \theta_1,$$

is very pronounced. The reflection of the second order, for which

$$2\lambda = 2d \sin \theta_2,$$

is much less intense, and the other reflections diminish regularly in intensity as the order of reflection increases.

It will be noticed that θ_1 for the face (100) is 5·9°, θ_1 for the face (110) is 8·25°.

$$\frac{\sin 8{\cdot}25^\circ}{\sin 5{\cdot}9^\circ} = 1{\cdot}43 = \sqrt{2} = \frac{d_{(100)}}{d_{(110)}}.$$

[*] The angles given in Table I are those at which the ionisation chamber is set. These angles can be determined with much greater accuracy than the angles of reflection which are half as great.

The spectra reflected from the face (111) have a very different appearance. The second spectrum is now much more pronounced than the first. The reason for this appears when the arrangement of the planes parallel to this face is taken into consideration (see fig. 1 B). Instead of the successive planes being identical in character sodium and chlorine planes alternate.

The first spectrum corresponds to the spacing $d_{(111)}$ of chlorine to chlorine planes. The reflection corresponding to this spacing is spoilt, however, by the interposition of the lighter sodium planes, exactly intermediate with the chlorine ones.

The effect of this is to weaken all the odd spectra in comparison with the even. If the sodium planes were so light as to be non-effective, the odd spectra would be of normal strength. If they became as effective reflecting agents as the chlorine planes, the odd spectra would disappear entirely, for one would have a succession of identical planes at a distance $d_{(111)}/2$. What is actually the case represents an intermediate state of affairs.

This very simple case has been entered into in some detail in order to make clear what follows. Two crystals will now be considered which present slightly more complicated features.

Zinc Blende, ZnS.—This case is of especial interest as it is the crystal originally employed by Laue in his investigations. The spectra for the principal faces were obtained by W. H. Bragg, and published in our joint paper[*] on "The Structure of the Diamond," where a short account of the crystalline structure was given. The arrangement of the heavy zinc atoms of the crystal is revealed by the Laue photographs, they lie on a face-centred cubic lattice as do the chlorine atoms in sodium chloride. This conclusion may be verified by a comparison of the dimensions of the spacing for rock salt and zinc blende. For if the atoms of the metal are in both cases arranged on the same type of cubic lattice, then the relative dimensions of the lattices can be found by comparing the molecular volumes of the two substances. The distance $2a$ should be proportional to the cube root of the molecular volume, and therefore $\sin\theta_1$ inversely proportional to this quantity. This is found to be so.

The zincs are arranged on a face-centred cubic lattice. Let this lattice be supposed to suffer a translation in the direction of a cube diagonal (DF in fig. 2), the lattice remaining parallel to itself. The extent of the translation is just such as to bring the point D to the centre of the small cube D*d*QCLO*n*N of which it was formerly a corner. The new points thus arrived at represent the positions of the sulphur atoms.

The principal planes then have the arrangement depicted in fig. 2B.

Referring to Table I the spectra of (110) are alone normal; for (100) the odd spectra are small compared with the even, exactly as for rock salt (111). The (111) planes are of a new type, inasmuch as the sulphur planes are so placed as to tend to destroy the second spectrum as compared with the first and third. The effect of this is very noticeable in the spectra. It is to be noticed especially that the trigonal axis perpendicular to the planes (111) of this crystal is made polar by this arrangement of the atoms. Passing along it in one direction, the pairs of planes Zn and S are encountered in a different order to when passing in the opposite direction. This accounts for the fact that zinc blende belongs to the ditesseral polar class of the cubic system.

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[*] 'Roy. Soc. Proc.,' A, vol. 89, p. 277.

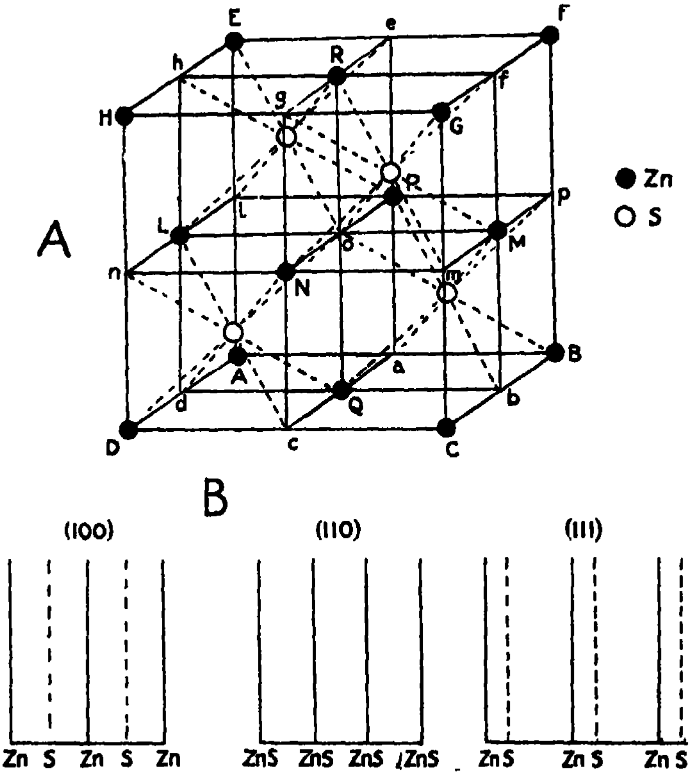

Fig. 2.

Fluor spar, CaF_2, presents a very analogous case. Here again the atoms of the metal are arranged on a face-centred cubic lattice. The normality of the (110) spectra indicates that the fluorine atoms lie in the (110) planes of the lattice formed by the calcium atoms, and we therefore place them at the centres of the eight cubes into which the large cube ABCDEFGH is divided in fig. 1. Since we now have twice as many fluorine as calciums, each of the small cubes must have a point at its centre, instead of one half of the cubes, as in the case of zinc blende. This raises the symmetry again to that of the holohedral cubic class. The arrangement of planes parallel to the principal faces is shown in fig. 3.

On comparing the spectra of fluor spar (Table I) with those of zinc blende, it will be seen that for fluor spar (100) the spectrum analogous to the first in zinc blende is now entirely absent. Similarly the second (111) fluor spar is absent, though a faint second (111) exists for zinc blende. This must mean that the planes F_2 are equivalent to the planes Ca in reflecting power, and so the odd spectra from the (100) face of fluor spar are annihilated.

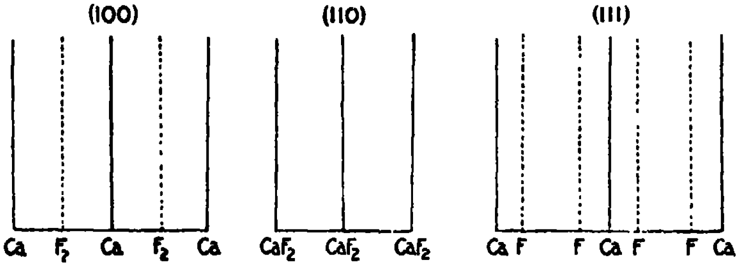

FIG. 3.

This is an indication of a general law which will be tested much more fully later in the paper. This law states that "the diffracting power of an atom is proportional to its atomic weight." We have already seen for the case of potassium chloride that two atoms of nearly equal atomic weights diffract equally. This law can now be extended to such cases where we are balancing a single atom of calcium (at. wt. 40) against two atoms of fluorine $(19+19=38)$.

The spectra for diamond are given in our paper on the structure of that crystal (*loc. cit.*). In diamond carbon atoms are substituted for both the zincs and sulphurs of zinc blende. This raises the symmetry to that of the holohedral cubic class. If we imagine the zincs and sulphurs of zinc blende to become equal in diffracting power, the spectra would assume the form characteristic of diamond. The first (100) entirely disappears, as does the second (111).

For these four structures given here, the symmetry fixes exactly the position of each atom. Every atom is in such a position that the forces on it must obviously be in equilibrium. For instance, each sulphur in zinc blende is immediately surrounded by four zincs symmetrically placed so as to form the corners of a tetrahedron, of which the sulphur represents the centre of figure. The more distant zincs can be also seen to be so situated as to ensure that their actions on the sulphur atoms balance. The same is true for the other crystals. If we assume that the atoms themselves have no polarity and that their attractions and repulsions of neighbouring atoms are not a function of the orientation of the atoms, it follows that the structures assigned to crystals are those in which there is equilibrium. The stability or otherwise of this equilibrium is another matter.

We will now consider a case for which this does not hold good. The atoms in this case are no longer at the "centres of the figure" of the structure, they are displaced by a very large amount from these ideal positions, and their exact situation is not fixed by the symmetry.

Iron Pyrites, FeS_2.—Cubic. Symmetry Tesseral Central. The spectra of iron pyrites are given in Table I. It will at once be evident that they are of a very much more complicated nature those of fluor spar or zinc blende. A comparison of the molecular volumes and reflection angles of this crystal and those considered above shows that the iron atoms are again present in such numbers as they would be if arranged on a face-centred lattice. Since the first spectra are also in the positions to be expected for such a lattice, it is clear that this lattice is again the basis of the structure.

If the iron atoms were on the face-centred lattice of figs. 1 and 2 and the sulphur atoms at cube centres, the structure would be similar to that of fluor spar. Since sulphur is approximately of half the atomic weight of iron, just as fluorine is of calcium, one would expect the spectra of these two crystals to resemble each other. This is far from being the case, and we must alter the structure in such a way as to explain the observed spectra.

The spectra for the face (100) are very peculiar. The first spectrum is pronounced, the second and third are absent, the fourth and fifth are of normal size compared to the first. This suggests that the arrangement of the pyrites (100) planes is somewhat similar to that of the planes (111) of fluor spar (compare fig. 3).

In order that this may be so we must displace the sulphurs from their positions at the cube centres. Normally each small cube (as in fig. 2) possesses four trigonal axes intersecting in the centre of the cube. If the sulphur atom is moved, from its position at the cube centre, this high symmetry is degraded, and some of the trigonal axes disappear. Therefore moving the sulphur atoms from the centre involves the sacrifice of some of the elements of symmetry. Four trigonal axes intersect in each iron atom, and of them one at least must be retained, in order that the crystal may be of the cubic system, and the iron atoms may remain identical with each other. This involves the retention of one trigonal axis as a diagonal of each small cube (fig. 4), and it is, therefore, along this diagonal that the sulphur must be displaced. It must lie on the diagonal, for if not each small cube would contain three atoms of sulphur arranged around the trigonal axis, while we know it only contains one.

It seems to follow, therefore, that the displacement of the sulphur atoms must be carried out in the following way. One diagonal of each cube is chosen to be preserved as a trigonal axis, the choice taking place in such a way that none of the trigonal axes intersect. Each of these diagonals then has an iron atom at one end and a vacant cube corner at the other. Then the sulphur atoms must be displaced along the selected diagonals on which they lie. All must be displaced towards the neighbouring iron atoms, or all away from them. The amount of the displacement is a variable quantity at our disposal. When this has been done, the structure possesses the symmetry characteristic of iron pyrites (Tesseral Central). The projection of the

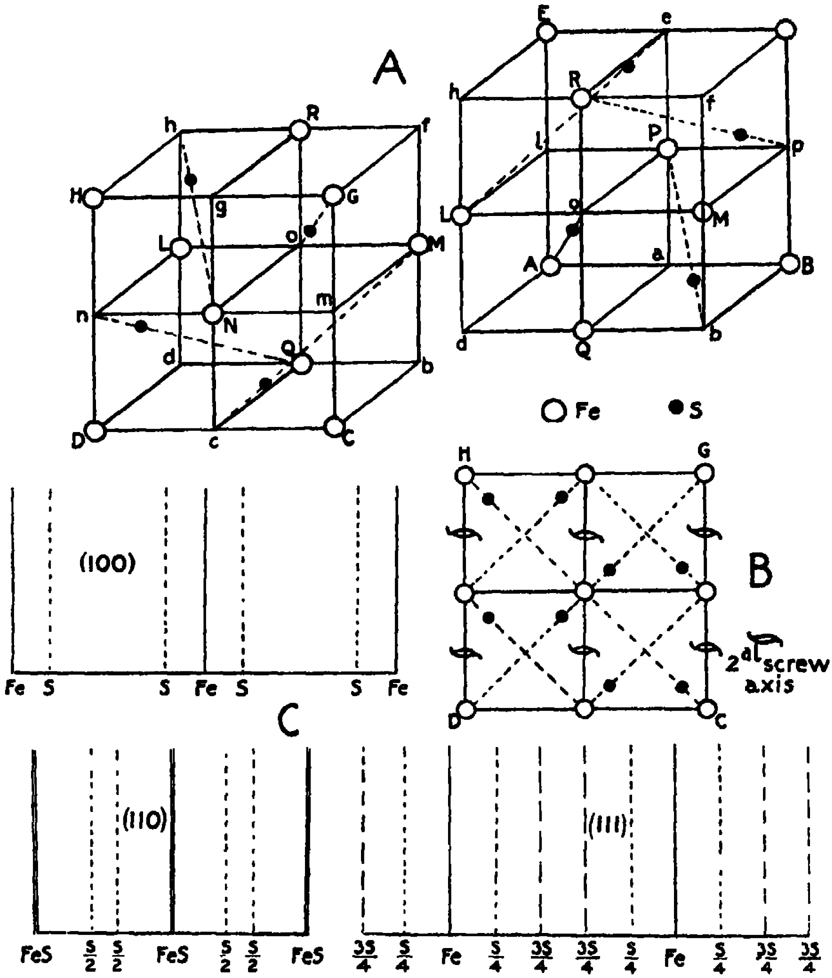

Fig. 4.

atoms in the unit cube ABCDEFGH* as projected on the plane DHGC is shown in fig. 4B and it is clear that the tetragonal axes perpendicular to this face have been destroyed and that only digonal axes remain. The centres of symmetry are situated at every cube corner. Let the sulphur atom be displaced along the axis until it divides the diagonal in the ratio 4 to 1, the displacement taking place towards the unoccupied cube corner. The arrangement of the principal planes which then exists is shown in fig. 4C.

Being situated at 1/5th $d_{(100)}$ from the iron planes, the sulphurs will tend to cut out both the second and third (100) spectra. For if they were at $\frac{1}{4}$ $d_{(100)}$ from the iron planes, they would just cut out the second spectrum; if at 1/6th $d_{(100)}$, they would cut out the third. In the plane (110), the presence midway between planes FeS of the pair of planes S/2 will tend to raise the second (110) spectrum as compared with the first. For the planes (111) the first spectrum will be small compared with the second, and the fifth will be abnormally large. This qualitative comparison of the spectra with those actually obtained will demonstrate that the position of the sulphur atom which we have assigned to it is not far from the truth.

Since in the case of iron pyrites the positions of the sulphur atoms are not fixed by the conditions of symmetry, the more or less qualitative analysis so far employed can only suggest their positions approximately. In order to fix these positions with accuracy, it is necessary to develop some quantitative comparison of the intensities of the first, second, third, fourth, and fifth spectra.

The Quantitative Comparison of Spectra.

In the first place, experiments seem to indicate that the diffracting power of an atom varies as its atomic weight. The ratio of the diffracting power of two atoms is taken to be the ratio of the amplitudes of the diffracted wavelets which each would send out in identical circumstances, the same exciting wave passing over them. In the case of fluor spar, it has already been seen that the two fluorine atoms, whose combined atomic weights amount to 38, equal in diffracting power the single calcium of atomic weight 40. The series of carbonates isomorphous with calcite provide another case, which illustrates this law very clearly.

The spectra assign a very simple structure to these compounds, which belong to the rhombohedral holohedral crystal class. The exact structure of the calcite crystal is immaterial for present purposes; it is given in detail at the end of this paper. It is only necessary to note that, perpendicular to the trigonal axis, the planes are evenly spaced, and contain alternately calcium atoms and groups of the composition CO_3 (*cp.* fig. 7). As is to be expected from its close structural relationship with calcite, sodium nitrate gives spectra in every way analogous to those of the calcite class. It is therefore included in the table below.

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* In fig. 4 the cube ABCDEFGH has been represented as divided into halves, in order to make the disposition of trigonal axes (the dotted diagonals) more clear. The lettering will show how the cubes are to be connected.

In Table II are given the relative intensities and angles for the first, second, third, and fourth spectra from faces (111) of the compounds $NaNO_3$, $CaMg(CO_3)_2$, $CaCO_3$, $MnCO_3$, $FeCO_3$. As before, the angles are those of the ionisation chamber, or double the glancing angles of reflection. It will be seen that, as the atomic weight of the metal approaches that of the group CO_3, the first spectrum becomes smaller compared with the second. This means that the planes R″ and CO_3 are becoming more nearly equal in diffracting power. Iron and manganese, with atomic weight of 56 and 55 respectively, must have approximately the same diffracting power as the group CO_3, for which $C+3O = 12+48 = 60$, for the first spectrum has vanished in the case of $FeCO_3$ and $MnCO_3$. This must mean that diffracting power is proportional to atomic weight.

Table II.

(111) face, calcite class. Pd rays.

Spectra.	1st.	2nd.	3rd.	4th.
Na NO_3 23 62	100 11·6°	50 23·2°	0 —	0 —
CaMg $(CO_3)_2$ 32 60	100 12·8°	100 24·5°	0 —	8 52·2°
Ca CO_3 40 60	30 11·2°	100 23·4°	0 —	14 48·2°
Mn CO_3 55 60	0 —	100 25·9°	0 —	10 52·5°
Fe CO_3 56 60	0 —	100 26·2°	0 —	0 —

Secondly, it has been seen that, when the rays are reflected from a series of planes which are regularly spaced and identical in all respects, the successive spectra diminish in intensity in a perfectly orderly manner. It can be further stated that, for all cases where the planes are of this type, the intensities of the successive spectra are approximately in the same ratio. If the first spectrum has an intensity 1, the second, third, fourth, and fifth spectra have intensities 0·2, 0·07, 0·03, 0·01. These numbers are only suggested as being very rough approximations. The faces (100) and (110) rock salt, (110) fluor and zinc blende, (100) and (110) diamond, are cases where the spectra intensities are of this normal type (see Table I).

Let us now suppose that we are considering the reflection from faces of a crystal of a binary compound, composed of two elements, A and B, of atomic weights m_1 and m_2. The successive planes parallel to any one face may be identical in all respects, and contain both A and B atoms. Or, as often happens, they may alternately consist of A atoms alone and B atoms alone. In the first case the spectra will be of the normal type. The identical planes of composition AB may be considered as consisting of two sets of coincident planes of composition A and B. Now, let us suppose that the whole set of B planes is slightly shifted relatively to the A planes, so that (1) passes into (2), fig. 5. The distance D remains the same as before; the shift of the B planes is equal to D/n.

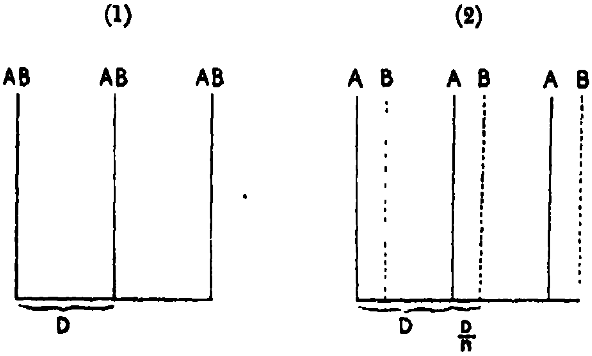

FIG. 5.

This causes the wavelets from the B planes to be in a different phase to the wavelets from the A planes. All other conditions remain the same; the same incident wave passes over the planes as would if they were coincident; it is absorbed to the same extent on reaching a corresponding depth; the emergent reflected wave is also equally absorbed by the superficial layers of the crystal. We can therefore compare with fairness the strength of the reflection from (1) with that from (2) under similar conditions, by comparing the reflection by a single plane AB with that by the pair of planes A and B. The amplitude of the wavelet reflected from planes A is proportional to m_1. That from planes B is proportional to m_2. They differ in phase by $2\pi/n$ for the first spectra, $4\pi/n$ for the second, and so on. Thus we may institute the following comparison:—

Order of spectrum.	Intensities.	
	Case I.	Case II.
1	$1\,(m_1+m_2)^2$	$1\,[m_1^2+m_2^2+2m_1m_2\cos(2\pi/n)]$
2	$0{\cdot}2\,(m_1+m_2)^2$	$0{\cdot}2\,[m_1^2+m_2^2+2m_1m_2\cos(4\pi/n)]$
3	$0{\cdot}07\,(m_1+m_2)^2$	$0{\cdot}07\,[m_1^2+m_2^2+2m_1m_2\cos(6\pi/n)]$
4	$0{\cdot}03\,(m_1+m_2)^2$	$0{\cdot}03\,[m_1^2+m_2^2+2m_1m_2\cos(8\pi/n)]$
5	$0{\cdot}01\,(m_1+m_2)^2$	$0{\cdot}01\,[m_1^2+m_2^2+2m_1m_2\cos(10\pi/n)]$

The intensity of the spectrum is taken to be proportional to the square of the amplitude of the resultant reflected wavelet.

It is obvious that this reasoning may be extended to cases where the arrangement of planes is more complicated. It is only a question of finding the resultant of several wavelets of known amplitudes and phase relations, as against that of finding the resultant of two. We are now in a position to calculate theoretically the spectrum intensities to be expected for any structure assigned to a crystal. In this calculation the following assumptions are made:—

1. The diffracting power of an atom is proportional to its atomic weight.

2. The "normal" spectra reflected from a simple series of identical planes have intensities in the ratio

$$1, \quad 0{\cdot}2, \quad 0{\cdot}07, \quad 0{\cdot}03, \quad 0{\cdot}01.$$

3. Neighbouring atoms diffract independently of each other.

This last has been tacitly assumed above.

The results of the calculation are given in Table III (p. 482).

It will be seen by these results that the calculated and observed intensities obviously run parallel to each other. Taking into account the many experimental errors in the determination of the relative intensities, and the crude nature of the assumption which has been made, closer agreement could not be expected. The results certainly show that all the peculiar features of any set of spectra can be assigned to structural peculiarities of the crystal. If a certain spectrum is missing, or is unusually strong, a reason for it is found in the arrangement of the crystal planes.

Iron pyrites provides a good example. In order to account for the peculiar fact that the (100) planes have no second or third spectrum, we place the sulphur atoms in such a position as to divide the diagonal in the ratio 1 : 4. When the sulphur atoms are placed here the structure of the crystal is illustrated in fig. 4.

In this figure (A) represents the unit cube of the structure which is afterwards repeated without change parallel to itself. It is the unit of the pattern, and its sides are the primitive translations of the group. Four

Table III.

Spectra.	Observed.					Calculated.				
	1st.	2nd.	3rd.	4th.	5th.	1st.	2nd.	3rd.	4th.	5th.
Rock salt—										
(100)	100	30	7	—	—	100	20	7	3	
(110)	100	24	7	—	—	100	20	7	3	
(111)	20	100	0	6	—	22	100	2	15	
Fluor spar—										
(100)	0	100	0	13	—	0	100	0	15	
(110)	100	16	6	—	—	100	20	7		
(111)	100	0	10	9	3	100	0	7	11	1
Zinc blende—										
(100)	40	100	0	0	—	53	100	5	3	
(110)	100	25	7	0	—	100	20	7		
(111)	100	5	8	—	—	100	4	11	8	
Iron pyrites—										
(100)	100	0	0	14	4	100	0	0	8	5
(110)	100	50	—	—	—	100	50	11	13	
(111)	80	100	50	0	22	78	100	35	0	21
Ideal spectrum						100	20	7	3	1

iron atoms and eight sulphurs are associated with it. The cube is represented as being in two halves, in order to make the structure more clear. The diagonals which are marked are trigonal axes of the system. Every corner of the eight small cubes into which the structure is divided is a centre of symmetry. Through each side centre of these cubes passes a single digonal screw axis, parallel to one of the cube axes. Fig. 4B represents the structure as projected on a plane (100), and it is evident that this face has a digonal axis, and not a tetragonal axis, perpendicular to it.

The features are those characteristic of the crystal class to which iron pyrites belongs.

The way in which the spectra of iron pyrites have been calculated from the assumptions given above will be entered into rather fully here, as this case is a good instance of the quantitative analysis of strength of spectra.

The arrangement of planes parallel to the three principal faces of the crystal is given in fig. 4C, the sulphurs being placed so as to divide the diagonal in the 1 : 4 ratio. This is done in order to account for the fact that the face (100) has no second and third order spectra. For calculation then gives for the relative amplitudes of the first, second, and third spectra

$$56+2\{32\cos(2\pi/5)\} = 56+21 = 77.$$
$$56+2\{32\cos(4\pi/5)\} = 56-61 = -5.$$
$$56+2\{32\cos(6\pi/5)\} = 56-61 = -5.$$

It is obvious that when these amplitudes are squared and multiplied by the factors for the normal spectrum, the second and third spectra will be vanishingly small compared to the first.

The planes parallel to (111) have a peculiar arrangement; their spectra can be worked out by the help of fig. 6. The three circles in the figure have radii proportional to Fe = 56, S/4 = 8, 3S/4 = 24. Each circle is divided into five by the lines $OA_1B_1C_1$, $OA_2B_2C_2$, etc. The angle $A_1OA_2 = 2\pi/5 = 72°$. The wavelets which are reflected from one of these groups of planes and which go to build up the first spectrum have relative amplitudes and intensities represented by OB_4, OA_5, OC_1, OA_2, OB_3, these being due to the planes 3S/4, S/4, Fe, S/4, 3S/4 of a group. The amplitudes of these waves are 24, 8, 56, 8, 24 respectively, and their resultant is

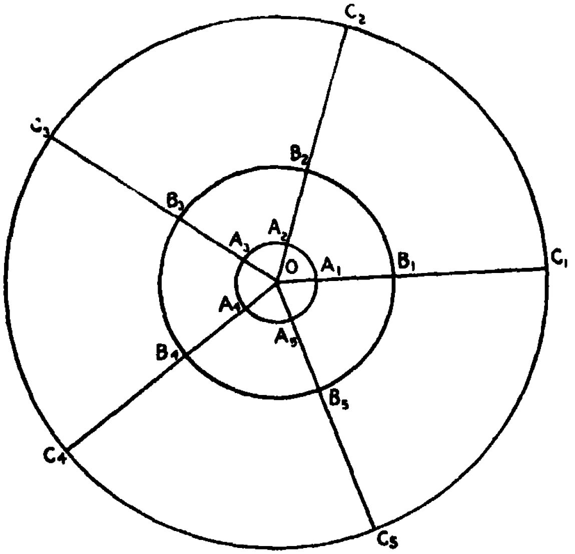

FIG. 6.

$$56+2{\cdot}8\cos(2\pi/5)+2{\cdot}24\cos(4\pi/5) = 56+5-38 = 23.$$

For the second spectrum the resultant of OB_2, OA_4, OC_1, OA_3, OB_5, is equal to $(56-13+15) = 58$. For now the 3S/4 planes are $8\pi/5$ out of phase with the Fe planes, and the S/4 planes $4\pi/5$ out of phase. The third spectrum is the resultant of these same components, and the amplitude of the reflected wave is proportional to 58. For the fourth we have the resultant of

OB_4, OA_5, OC_1, OA_2, OB_3, as for the first spectrum. The resultant is again proportional to 23. For the fifth spectrum obviously all the components are in phase. The amplitude is measured by $56+64 = 120$.

Thus the amplitudes of these spectra are in the ratio

$$23 : 58 : 58 : 23 : 120.$$

So far, therefore, their intensities are in the ratio

$$(23)^2 : (58)^2 : (58)^2 : (23)^2 : (120)^2.$$

And when multiplied by the factors for the normal spectrum, these ratios become

$$(23)^2 : 0{\cdot}2\,(58)^2 : 0{\cdot}07\,(58)^2 : 0{\cdot}03\,(23)^2 : 0{\cdot}01\,(120)^2,$$

or

$$78 : 100 : 80 : 2 : 21.$$

If the sulphur atoms are placed so as to divide the cube diagonal in the ratio 1 : 3 (see fig. 7), the strengths of the spectra, as calculated above, become

$$100 : 56 : 38 : 0 : 8.$$

If they divide the diagonal in the ratio 1 : 5, they can be calculated to be

$$19 : 100 : 24 : 7 : 17.$$

Therefore, we have the following comparison :—

Ratio.	Intensities.				
1 : 3	100	56	38	0	8
1 : 4	78	100	35	2	21
1 : 5	19	100	24	7	17
Observed intensities......	75	100	50	0	22

The 1 : 4 ratio seems, therefore, to be very nearly the true one. These three situations for the sulphur atom are very close. If d = length of cube diagonal, the distance of the sulphur atom from the cube corner is $0{\cdot}25d$, $0{\cdot}20d$, $0{\cdot}17d$ for the three cases. It seems reasonable to conclude from these figures that this distance lies between $0{\cdot}19d$ and $0{\cdot}21d$, or that the position of the sulphur atom on the diagonal may be found to 1 or 2 per cent. of the length of the diagonal.

The crystalline structure of hauerite, MnS_2, is, as far as has been investigated, identical with that of iron pyrites. The (100) planes have a strong first spectrum and no second and third. The planes (111) have the first, second, and third spectra in the ratio 32 : 100 : 50. As the only crystals available were small no great reliance is to be placed on these figures except as indicating that the structure is very nearly that of iron pyrites. This is surprising, considering the great difference in the molecular volume of hauerite, 34·4, as compared with that of pyrites, 23·5.

All the calculated spectra in Table III have been worked out in this way. Let it be repeated here that the factors representing the strengths of the normal spectra are only intended to be rough approximations. They do not represent an unaltering relation between the relative strengths of the spectra of different orders for all substances. This relation probably varies with the substance and with the angle of reflection of the first spectrum. They are merely introduced in order to make it clear that the peculiarities of the spectra obtained from the crystals dealt with here can be satisfactorily explained by the structures assigned to them.

Fluor spar belongs to the holohedral class of the cubic system, and the structure we would assign to it is of that symmetry. Zinc blende is of the ditesseral polar class, and this agrees with its structure as indicated by the spectrometer. The peculiar position of the sulphurs in the structure of pyrites would suggest that the crystal might be expected to show that strong evidence of its tesseral central symmetry which is so distinct in crystals of this substance. But in the case of rock salt, the spectrometer gives no indication whatever that the atoms are arranged in any but the highly symmetrical structure of fig. 1. Yet there is strong evidence that rock salt really belongs to the holoaxial class of the cubic system. If this is so, then the distortion of fig. 1 which causes this degradation of symmetry must be very slight. If the sulphur atoms in iron pyrites were very nearly at the cube centres, but not quite, the spectra would not show this, while it is quite possible that etched figures might reveal the true class of the crystal. It seems that something of this kind must be the case for rock salt. However, the most simple distortion which yet preserves the equivalence of all sodium and chlorine atoms reduces the symmetry from the holohedral to the tetartohedral class of the cubic system, not to the holoaxial class.

The Structure of Calcite.—The structure of calcite has been referred to already. Table IV gives the angles of reflection and the relative intensities of the spectra from faces (111), (100), $(\bar{1}10)$, (110), $(\bar{2}11)$. Fig. 7 displays the structure these spectra indicate. The rhomb ABCDEFGH has sides parallel to the cleavage planes of the crystal, the value of the angle EAB being 102°. With the rhomb are associated four atoms of calcium, and so four molecules of calcium carbonate. The mass of a molecule is $1{\cdot}64 \times 10^{-24} \times 100$ grm., the density of calcite 2·71, therefore the volume of this rhomb must be

$$\frac{1{\cdot}64 \times 10^{-24} \times 100}{2{\cdot}71} \times 4 = 242 \times 10^{-24} \text{ c.c.}$$

From this we can calculate that the length of its edge is $6{\cdot}38 \times 10^{-8}$ cm.

This gives for $d_{(100)}$ calcite the length $3{\cdot}04 \times 10^{-8}$ cm. The angle θ at which reflection is to be expected is therefore given by

$$\lambda = 2d \sin \theta,$$

$$0{\cdot}576 \times 10^{-8} = 2(3{\cdot}04 \times 10^{-8}) \sin \theta,$$

$$\sin \theta = 0{\cdot}0947,$$

$$\theta = 5{\cdot}43^\circ.$$

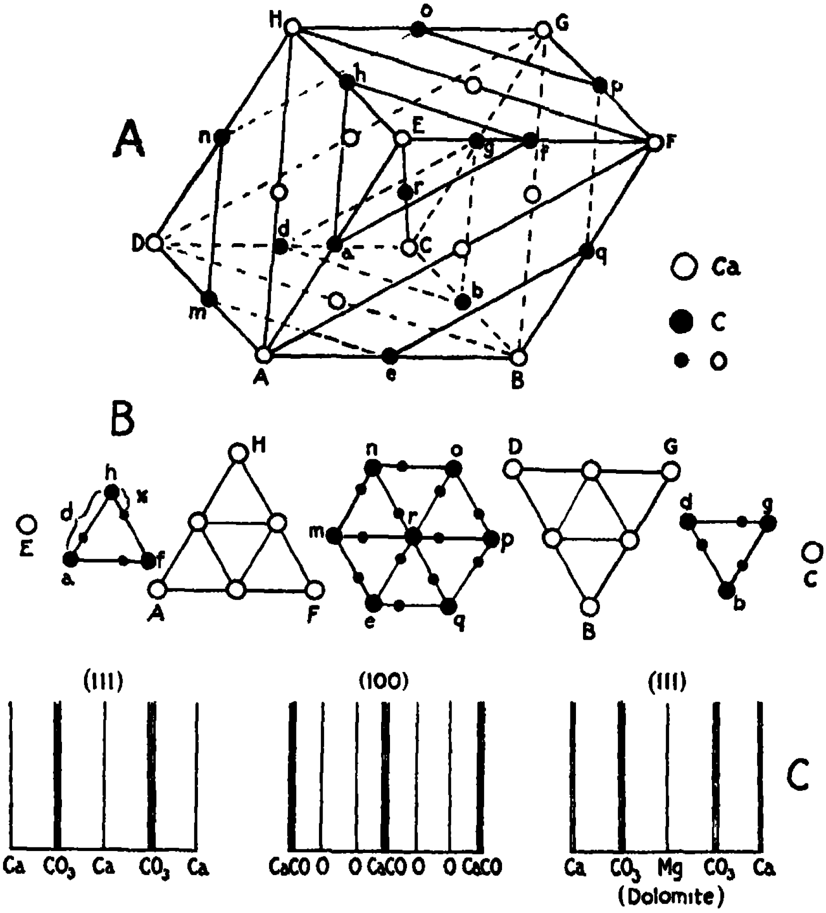

FIG. 7.

The reflection is actually found at 5·35°. This shows that the correct number of $CaCO_3$ molecules has been assigned to the rhomb. The (111) spectra of the series of carbonates isomorphous with calcite have already been dealt with. They show that the alternate planes parallel to (111) planes have the composition $CaCO_3$.

In the simple structure given in fig. 7A* the symmetry alone fixes the positions of the calcium and carbon atoms, calcite belonging to the rhombohedral holohedral class. But the oxygen atoms have one degree of freedom: their distance from the nearest carbon atom in the (111) plane can be altered without changing the symmetry. As in the case of the sulphurs of iron pyrites, a quantitative investigation is necessary in order to determine the exact position of these atoms. We will employ the (100) spectra for this purpose. In Table V will be found the intensities of spectra reflected from the (100) faces of $NaNO_3$, $CaMg(CO_3)_2$, $CaCO_3$, $MnCO_3$, $FeCO_3$. It

Table IV.—Spectra yielded by Calcite ($CaCO_3$). Pd rays.

(111)	30 11·2°	100 23·4°	0 33·7°	14 45·5°
(100)	100 11·2°	20 22·5°	20 33·7°	0 45·5°
($\bar{1}$10)	100 13·0°	66 26 8°	0 —	
(110)	100 17·4°	— —	— —	
(211)	100 23·2°	6 48°	0 —	

Table V.

	Observed.				Calculated.			
Sodium nitrate, $NaNO_3$—								
(100)	100	10	6	3				
(111)	100	50	—	—	100	75	7	12
Dolomite, $(CaMg)(CO_3)_2$—								
(100)	100	14	13	3				
(111)	100	100	0	8	50	100	3	15
Calcite, $CaCO_3$—								
(100)	100	20	20	9	100	11	18	8
(111)	30	100	0	14	20	100	1	15
Rhodochrosite, $MnCO_3$—								
(100)	100	26	15	0				
(111)	0	100	0	10	0	100	0	15
Chalybite, $FeCO_3$—								
(100)	100	43	40	28				
(111)	0	100	0	—	0	100	0	15

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* In fig. 7A, the calcium and carbon atoms alone are represented, for the sake of clearness. Fig. 7B gives a series of sections perpendicular to the trigonal axis EC of the crystal, and here the oxygen atoms are in position.

will be seen that they differ in character from crystal to crystal. For calcite, the second spectrum is very small compared with the first, for chalybite it is very large. We will try what effect the position of the oxygen atoms has upon the intensity of the (100) spectra of calcite.

The position of the oxygen atom may be defined by the ratio of the distance x to the distance d in fig. 7B. The arrangement of the (100) planes is shown in fig. 7C, and here the ratio of the distance between a CaCO plane and an O plane, to that between successive CaCO planes, is equal to x/d. The planes CaCO have mass $40+12+16 = 68$. The planes O have mass 16. The spectra intensities for various values of x/d for calcite are calculated to be as follows :—

	1st.	2nd.	3rd.	4th.	5th.
Normal spectrum . .	100	20	7	3	1
x/d = 0·25	100	6	7	7	1
„ = 0·30	100	11	18	8	
„ = 0·33	100	20	30	3	1
„ = 0·35	100	30	31	2	
„ = 0·40	100	67	23	8	6

The second, third, and fourth spectra are in general so small that it is very difficult to estimate accurately their intensities. The results for calcite seem to show that the ratio x/d is very nearly 0·30. As for the other crystals, x/d for dolomite seems to be rather smaller than this. For chalybite it is certainly much larger, about 0·37, though it is difficult to account for the fourth spectrum of that crystal. For rhodochrosite it seems to be about 0·34. In general the value of x approximates to $d/3$.

It is tempting to consider that in dolomite the arrangement of planes perpendicular to the trigonal axis may be Ca–CO_3–Mg–CO_3. This would give the crystal the right symmetry (rhombohedral tetartohedral), the digonal axes being destroyed by the substitution of magnesium atoms for half the calcium atoms.* It would then be expected that a spectrum would be found corresponding to the distance Mg–Mg planes in dolomite, *i.e.* a spectrum at an angle half as small as the usual angle (12–13° chamber) for this series. No trace of such a spectrum has as yet been found, but it would be easy to miss it. In the first place the glancing angle for Pd rays would be only 3°, in the second place this spectrum would be small compared with the first. More careful measurements of crystals will, it is hoped, settle these doubtful points.

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* Compare Barlow and Pope, 'Trans. Chem. Soc.;' vol. 98, p. 1552.

In conclusion, I wish to express my thanks to Dr. Hutchinson, who has supplied from the mineralogical collection at Cambridge most of the crystals required for these investigations. For a quantitative comparison of spectra intensities fine specimens of the various crystals are a necessity, and it is due to his kindness that such specimens could be used. To Mr. Peirce I am indebted for much assistance with the observations.

I have also to thank the authorities of the University of Leeds for permission to carry out the experiments in the Physical Laboratories, where I had the opportunity of working with one of the original X-ray spectrometers.

Ship Resistance: The Wave-making Properties of Certain Travelling Pressure Disturbances.

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1. In previous papers[*] I have investigated the wave-making resistance of a ship by comparing it with a certain simple type of pressure disturbance travelling over the surface of the water. In a recent paper[†] on the effect of form and size on the resistance of ships, by Messrs. Baker and Kent of the National Physical Laboratory, reference is made to this point of view. The main work of these authors consists in the examination of model results and the deduction of empirical formulæ of practical value. In addition, they connect the wave-making properties with the pressure distribution and have obtained graphs of the latter for various ship forms under certain conditions; these curves show a range of negative pressure, or defect of pressure, between the positive humps of excess pressure corresponding to the bow and stern. The authors remark that this will have an effect upon the wave-making, but conclude that it is sufficient for their purpose to be able to state that such pressure disturbances, as they have shown to exist when a ship is in motion, will produce waves which will vary more or less in accordance with the theory referred to above.

Under the circumstances it seems advisable to extend the mathematical theory by working out the wave-making properties of other distributions of pressure. Although no attempt has been made to connect the distribution directly with ship form, the following examples have been chosen with a view to general inferences which can be drawn in this respect. In particular, the distributions graphed by Baker and Kent can be represented, in type at least, by a mathematical expression for which the corresponding Fourier integral can be evaluated, so that one can compare the result with that obtained from simpler forms. Although the expression for the wave-making resistance becomes more complicated, it is not essentially different from that obtained previously; it appears in general to be built up of terms involving the same type of exponential e^{-a/v^2}, together with oscillating factors representing interference effects between prominent features of the pressure distribution.

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[*] 'Roy. Soc. Proc.,' 1909, A, vol. 82, p. 276; *also* 1910, A, vol. 84, p. 197; *also* 'Proc. Univ. Durh. Phil. Soc.,' 1910, vol. 3, p. 215.

[†] G. S. Baker and A. L. Kent, 'Inst. Nav. Arch.,' June, 1913.

2. We confine our attention to two-dimensional fluid motion. We may imagine it to be produced in a deep canal of unit breadth, with vertical sides, by the horizontal motion of a floating pontoon with plane sides fitting closely to the walls of the canal but without friction. We assume that, as regards *transverse* wave-making, this is effectively equivalent to some travelling distribution of pressure impressed upon the surface of the water.

Let Ox be in the direction of motion of the disturbance, and let y be the surface elevation of the water. Suppose the distribution of pressure to be given by

$$p = f(x). \tag{1}$$

For a line distribution we may suppose the disturbance to be inappreciable except near the origin and to be concentrated there in such a manner that the integral pressure P is finite, where

$$\mathrm{P} = \int_{-\infty}^{\infty} f(x)\, dx. \tag{2}$$

When this disturbance moves along the surface of water, of density ρ, with velocity v, the main part of the surface disturbance consists of a regular train of waves in the rear given by

$$g\rho y = -2\kappa \mathrm{P} \sin \kappa x, \tag{3}$$

where the length λ of the waves is

$$\lambda = \frac{2\pi}{\kappa} = \frac{2\pi v^2}{g}.$$

We can generalise this result for any form of pressure distribution $f(x)$, which is likely to occur, by the Fourier method. We have in general

$$g\rho y = -2\kappa \int_{-\infty}^{\infty} f(\xi) \sin \kappa (x-\xi)\, d\xi \tag{4}$$

$$= -2\kappa (\phi \sin \kappa x - \psi \cos \kappa x), \tag{5}$$

where $$\phi = \int_{-\infty}^{\infty} f(\xi) \cos \kappa\xi \, d\xi, \qquad \psi = \int_{-\infty}^{\infty} f(\xi) \sin \kappa\xi \, d\xi. \tag{6}$$

The mean energy per unit area of the wave motion given by (5) is $2\kappa^2(\phi^2+\psi^2)/g\rho$. Now the head of the disturbance advances with velocity v, while the rate of flow of energy in the train of waves is the group velocity $\frac{1}{2}v$; hence the net rate of gain of energy per unit area is $\frac{1}{2}v$ times the above expression for the energy. If we equate this product to Rv, then R may be called the wave-making resistance per unit breadth; and we have

$$\mathrm{R} = \kappa^2(\phi^2+\psi^2)/g\rho. \tag{7}$$

We have in each case to evaluate the complex integral

$$\chi = \phi + i\psi = \int_{-\infty}^{\infty} f(\xi) e^{i\kappa\xi} \, d\xi. \tag{8}$$

In the examples which follow, the integral has a finite, definite value which can be obtained in Cauchy's manner by integrating round a closed simple contour in the plane of the complex variable ξ. The function $f(\xi)$ is such that (i) it has no critical points other than simple poles in the semi-infinite plane situated above the real axis for ξ; (ii) it has no critical points on the real axis; and (iii) its value tends to zero as ξ becomes infinite. Further, the quantity κ is restricted to real, positive values. Under these conditions it can be shown[*] that

$$\int_{-\infty}^{\infty} f(\xi) e^{i\kappa\xi} \, d\xi = 2\pi i \Sigma \mathrm{A},$$

where $\Sigma\mathrm{A}$ is the sum of the residues of the integrand at the poles of $f(\xi)$ situated above the real axis. If a is a pole, A is given by the value of $(\xi-a)f(\xi)e^{i\kappa\xi}$ when $\xi = a$. Alternatively, in the following examples $f(\xi)$ is of the form $\mathrm{F}(\xi)/\mathrm{G}(\xi)$, none of the zeros of $\mathrm{G}(\xi)$ coinciding with those of $\mathrm{F}(\xi)$, and A is given by $\mathrm{F}(a)e^{i\kappa a}/\mathrm{G}'(a)$.

3. For the sake of comparison the results which have been obtained previously may be repeated briefly. If

$$p = f(\xi) = \frac{\mathrm{A}}{\xi^2+\alpha^2}, \tag{9}$$

the poles are at $\xi = \pm i\alpha$, of which the positive one alone concerns us. Hence we have

$$\chi = \int_{-\infty}^{\infty} \frac{\mathrm{A}e^{i\kappa\xi}}{\xi^2+\alpha^2} d\xi = 2\pi i \left| \frac{\mathrm{A}e^{i\kappa\xi}}{\xi+i\alpha} \right|_{\xi=i\alpha} = \frac{\pi}{\alpha} \mathrm{A}e^{-\alpha\kappa}. \tag{10}$$

Hence from (7) $$\mathrm{R} = \frac{\pi^2\mathrm{A}^2}{g\rho\alpha^2} \kappa^2 e^{-2\alpha\kappa} = \frac{\pi^2 g\mathrm{A}^2}{\rho\alpha^2 v^4} e^{-2g\alpha/v^2}. \tag{11}$$ [†]

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[*] Jordan, 'Cours d'Analyse,' vol. 2, § 270.

[†] *Cf.* Lamb, 'Hydrodynamics,' p. 391.

If A is a constant and independent of the speed v, the graph of R as a function of v rises to a maximum and then falls slowly but continually to zero as v increases indefinitely. Thus, for an assigned pressure disturbance of this type whose magnitude is independent of the speed, there is a certain speed beyond which the resistance R continually decreases.

On the other hand, if the pressure disturbance is that produced by the motion of a floating, or submerged, body, it is clear that it will depend upon the speed. Since we may suppose the pressures in question to be the excess or defect of pressure due to the speed, it seems a plausible first approximation to assume that the distribution is not altered appreciably in type and that the magnitude is proportional to v^2. Thus if in (11) we make A proportional to v^2 we obtain

$$\mathrm{R} = \text{const.} \times e^{-2ga/v^2}. \tag{12}$$

The value of R now tends to a finite limiting value as v increases indefinitely.

If the quantity A, specifying the magnitude of the pressure disturbance, varies as v^n, then the graph of R rises to a maximum for some finite value of v, provided n is positive and less than 2; the nearer n is to 2 the higher is the speed at which the maximum occurs. For the present we assume that n is equal to 2; in any case it does not affect the results of a qualitative comparison of different types of distribution.

The scope of the assumption may be illustrated by a certain case. Prof. Lamb* has worked out directly the wave-making resistance R due to a circular cylinder of small radius a, submerged with its centre at a constant depth f, and moving with uniform velocity v; he finds that R varies with the speed according to the law $v^{-4}e^{-2gf/v^2}$. If we attempt to represent the disturbance approximately by some equivalent surface pressure distribution, the type which suggests itself naturally is

$$p = \mathrm{A}(f^2 - x^2)/(f^2 + x^2)^2.$$

It can be shown† that this distribution, together with the assumption that A is proportional to v^2, leads to the same law of variation of resistance with speed.

4. In a certain sense the generalisation from a line disturbance to any diffused distribution of pressure may be regarded analytically as a case of interference; the final result is due to the mutual interference of the line elements into which we may analyse the given distribution. However, the idea of interference in ship waves has usually been associated, after the work

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* H. Lamb, 'Ann. di Matematica,' vol. 21, Ser. 3, p. 237.

† 'Roy. Soc. Proc.,' A, vol. 82, p. 300.

of W. Froude, with the superposition of bow and stern wave-systems, that is, when the whole system may be separated into two fairly distinct parts. I have represented this previously by a positive pressure system of type (9) associated with the bow, followed by a similar negative system associated with the middle of the run. Thus if l is the distance between the centres of the two systems we have in the present notation

$$p = \frac{A_1}{(\xi - \frac{1}{2}l)^2 + \alpha^2} - \frac{A_2}{(\xi + \frac{1}{2}l)^2 + \alpha^2}. \tag{13}$$

Substituting in (8) and evaluating the integrals we find

$$\phi = (A_1 - A_2)\, e^{-\alpha\kappa} \cos \tfrac{1}{2}\kappa l, \qquad \psi = (A_1 + A_2)\, e^{-\alpha\kappa} \sin \tfrac{1}{2}\kappa l.$$

Hence from (7)

$$g\rho R = \kappa^2 (A_1^2 + A_2^2 - 2A_1A_2 \cos \kappa l)\, e^{-2\alpha\kappa}. \tag{14}$$

The graph of R is a mean curve similar to (12) with oscillations superposed upon it, humps and hollows corresponding to minima and maxima of $\cos \kappa l$ or $\cos (gl/v^2)$.

It is of interest to note that if A_1 and A_2 are equal, we have

$$R = \text{const.} \times e^{-2\alpha\kappa} \sin^2 \tfrac{1}{2}\kappa l. \tag{15}$$

Thus, in a hollow, R would be actually zero if the two pressure systems were equal in magnitude. This, of course, follows at once from general principles; if we have a pressure system followed at a fixed distance by an equal and similar system, then there are certain wave-lengths and corresponding speeds for which the main regular waves due to the two systems cancel each other out exactly. A moving body which would produce such a state of affairs would be, in Lord Kelvin's phrase, a waveless pontoon. Of course, this does not occur in ship forms, and there are several reasons why it could not be expected to do so. In fact we have in general to suppose A_2 much less than A_1 in (13). However, it is conceivable that some change of form might give more effective interference effects of this kind and so deepen the hollows in the resistance curve, though possibly as a practical suggestion it may be subject to the same limitation as in other cases, namely, even if the wave-making resistance were lessened in this way probably the alterations would so increase frictional and other resistances that there might be no gain on the whole.

5. Baker and Kent have pointed out that in certain cases the pressure distribution at the entrance of a ship form is not simply a hump of excess pressure, but is a hump followed by a hollow of negative pressure. They assign to the interference of these two parts a certain subsidiary interference effect in the resistance which may become important when it coincides with

one due to the bow and stern systems. This follows on general grounds, and might be represented analytically as in § 4, but it is worth while examining other distributions with this character.

In the first place consider one which does not give the desired interference effect, namely,

$$p = \frac{A\xi}{\xi^2+\alpha^2}. \tag{16}$$

The graph has been drawn for certain numerical values of the constants and is curve A in fig. 1.

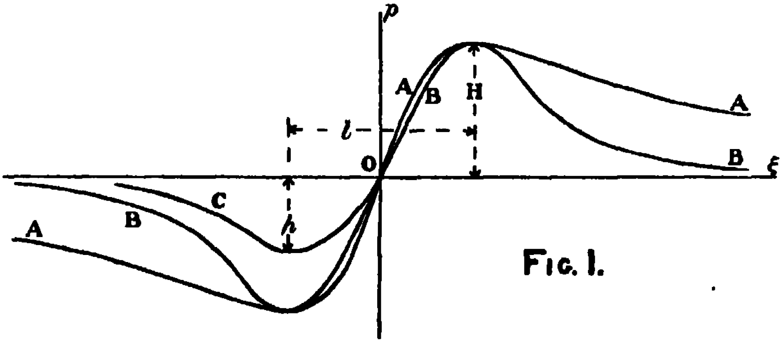

Fig. I.

We have $$\chi = \int_{-\infty}^{\infty} \frac{A\xi e^{i\kappa\xi}}{\xi^2+\alpha^2}\,d\xi = i\pi A e^{-\alpha\kappa}.$$

Hence, from (7) and (8),

$$\phi = 0; \qquad \psi = \pi A e^{-\alpha\kappa};$$

$$g\rho R = \pi^2\kappa^2 A^2 e^{-2\alpha\kappa}. \tag{17}$$

We have here the same form for R as a function of v as in (11) for the single hump of positive pressure; we do not get the interference effect which might have been expected. This may be explained by remarking that the pressure falls away from the maximum only slowly; in other words, the hump and hollow are not sufficiently pronounced for their individuality to show directly in the final formula. In the previous section, where the distribution is $1/(\xi^2+\alpha^2)$ instead of $\xi/(\xi^2+\alpha^2)$, the maximum and minimum are more pronounced and we get a typical oscillating term in the final result. This view may be confirmed by another example.

6. Consider

$$p = \frac{A\xi}{\xi^4+4\alpha^4}. \tag{18}$$

This distribution is graphed in curve B of fig. 1, arranged so as to have the same minimum and maximum as for (16); the curves A and B illustrate clearly the difference in question. Numerically, if ξ_0 is the position of the maximum, at $3\zeta_0$ the value of p from (16) has fallen to 3/5 of the maximum, while from (18) it has fallen to 1/7 of the same value.

The poles of the function in (18) are $\pm(1\pm i)\alpha$; thus from (8) we have

$$\begin{aligned}\chi &= 2\pi i \left| \frac{\xi e^{i\kappa\xi}}{\{\xi+\alpha(1-i)\}\{\xi+\alpha(1+i)\}\{\xi-\alpha(1-i)\}} \right|_{\alpha(1+i)} \\ &\quad + 2\pi i \left| \frac{\xi e^{i\kappa\xi}}{\{\xi-\alpha(1+i)\}\{\xi+\alpha(1+i)\}\{\xi-\alpha(1-i)\}} \right|_{-\alpha(1-i)} \\ &= \frac{i\pi}{2\alpha^2} e^{-\alpha\kappa} \sin \alpha\kappa.\end{aligned}$$

The wave-making resistance, R, is given by

$$4g\rho\alpha^4 \mathrm{R} = \kappa^2\pi^2 \mathrm{A}^2 e^{-2\alpha\kappa} \sin^2 \alpha\kappa. \tag{19}$$

We have now the oscillating factor $\sin^2\alpha\kappa$. There will be, for instance, a hump on the resistance curve when $2\alpha\kappa = \pi$, that is, when the half wave-length is equal to 2α. It may be noticed that this is nearly, but not exactly, the distance between the maximum and minimum of p; from (18) it follows that the latter distance is $2\alpha\sqrt[4]{(4/3)}$, or approximately $2{\cdot}15\alpha$.

We also have R exactly zero in the hollows in the resistance curve, a result which follows from the numerical equality of the positive and negative pressures at equal distances from the origin. We can make the negative pressures less by considering an unsymmetrical distribution.

7. Let the pressure be

$$p = \frac{\xi}{\xi^4 - \beta\xi + 4\alpha^4}. \tag{20}$$

In this case the graph would be as in fig. 1, with the curve B for positive ξ and the curve C for negative values.

If the poles of (20) are $a_1 \pm ib_1$ and $a_2 \pm ib_2$, we have

$$\left.\begin{aligned} a_1 + a_2 &= 0, \\ a_1^2 + b_1^2 + a_2^2 + b_2^2 + 4a_1a_2 &= 0, \\ 2\{a_1(a_2^2+b_2^2) + a_2(a_1^2+b_1^2)\} &= \beta, \\ (a_1^2+b_1^2)(a_2^2+b_2^2) &= 4\alpha^4. \end{aligned}\right\} \tag{21}$$

In forming the function χ by the previous method we have two parts. The part for the pole $a_1 + ib_1$ is

$$\begin{aligned} &2\pi i \left| \frac{\xi e^{i\kappa\xi}}{\{\xi-(a_1-ib_1)\}\{\xi-(a_2+ib_2)\}\{\xi-(a_2-ib_2)\}} \right|_{a_1+ib_1} \\ &= \frac{\pi}{b_1} \cdot \frac{(a_1+ib_1)e^{i\kappa a_1}e^{-\kappa b_1}}{(a_1-a_2)^2-(b_1^2-b_2^2)+2ib_2(a_1-a_2)}. \end{aligned} \tag{22}$$

There is also a similar expression corresponding to the pole a_2+ib_2; from (21) we see that the result can be written in the form

$$\chi = (A_1+iB_1)\,e^{i\kappa a_1}e^{-\kappa b_1}-(A_2+iB_2)\,e^{-i\kappa a_1}e^{-\kappa b_2}.$$

Hence for the resistance we have, from (7),

$$g\rho R/\kappa^2 = (A_1^2+B_1^2)\,e^{-2b_1\kappa}+(A_2^2+B_2^2)\,e^{-2b_2\kappa}$$
$$-2\left\{(A_1A_2+B_1B_2)\cos 2a_1\kappa-(A_2B_1-A_1B_2)\sin 2a_1\kappa\right\}e^{-(b_1+b_2)\kappa}. \qquad (23)$$

We notice how the presence of the smaller negative pressure complicates the mathematical expressions. On the other hand, all the terms are of the same type as in simpler cases; we have three terms involving the same exponential function, the third having an oscillating factor $\cos(2\kappa a_1+\epsilon)$, where

$$\tan\epsilon = (A_2B_1-A_1B_2)/(A_1A_2+B_1B_2). \qquad (24)$$

The humps and hollows on the curve for R will not coincide exactly with those obtained by graphing

$$e^{-2\kappa(b_1+b_2)}\cos(2a_1\kappa+\epsilon), \quad \text{with} \quad \kappa = g/v^2,$$

but the agreement will be sufficiently close for present purposes.

Accordingly, the maxima for R will be near speeds for which

$$2a_1\kappa+\epsilon = n\pi; \qquad n = 1, 3, 5, \ldots.$$

The corresponding speeds and wave-lengths are given by

$$v^2 = \frac{2ga_1}{n\pi-\epsilon}; \qquad \lambda = \frac{4\pi a_1}{n\pi-\epsilon}. \qquad (25)$$

In the previous case of symmetry, with the result in (19), the humps occur at wave-lengths $4a/n$, that is when the wave-length is equal to or an odd sub-multiple of a certain length; a similar statement in terms of velocity brings in the series $1, 1/\sqrt{3}, 1/\sqrt{5}$, etc. In the present case we see from (24) that this arrangement is somewhat disturbed by the presence of the phase ϵ, a quantity which may possibly be small compared with π. A complete algebraical study might be made, but possibly a simpler way would be to start from a graph of the pressure curve and carry out the integrations involved in (8) by graphical methods. We can also obtain information by working out some numerical examples; one may suffice at present, namely,

$$p = \frac{\xi}{\xi^4-180\xi+2419}. \qquad (26)$$

The pressure curve is of the form BC, shown in fig. 1, with

$$h/H = 0{\cdot}541; \qquad l = 10{\cdot}66.$$

Further, with the previous notation,

$$a_1 = -a_2 = 5, \qquad b_1 = 4, \qquad b_2 = \sqrt{34}.$$

Working out the numerical values from (22) we obtain for the resistance, omitting a constant factor,

$$R = 516e^{-8\kappa} + 353e^{-11\cdot06\kappa} - 857\cos(10\kappa - \epsilon)e^{-9\cdot83\kappa}, \tag{27}$$

with $\kappa = g/v^2. \qquad \tan\epsilon = 0\cdot017.$

We verify that in this case ϵ is, in fact, very small, consequently the simple relation between speeds at which there are humps is not appreciably altered. The absolute position of these humps on the R,v curve may be slightly displaced. For instance, the final hump occurs when 10κ is equal to π, that is when the half wave-length is equal to 10; on the other hand, the distance l between the maximum and minimum on the pressure curve is 10·66 units.

8. We turn now to more complicated distributions of pressure similar to those obtained by Baker and Kent, to which reference has already been made. We can build up a rational algebraic fraction which has at least the salient features of these curves; for instance, the graph of fig. 2 is represented by

$$p = \frac{2\xi^2 - \lambda^2 - \mu^2}{\xi^4 - (\lambda^2 + \mu^2)\xi^2 + \frac{1}{2}(\lambda^4 + \mu^4)}, \tag{28}$$

where λ and μ are constants. We have, on the curve,

$$OA = \lambda, \qquad OB = \sqrt{[\tfrac{1}{2}(\lambda^2 + \mu^2)]}, \qquad OC = \mu, \qquad AE = CD = 2/(\mu^2 - \lambda^2),$$
$$OF = 2(\lambda^2 + \mu^2)/(\lambda^4 + \mu^4).$$

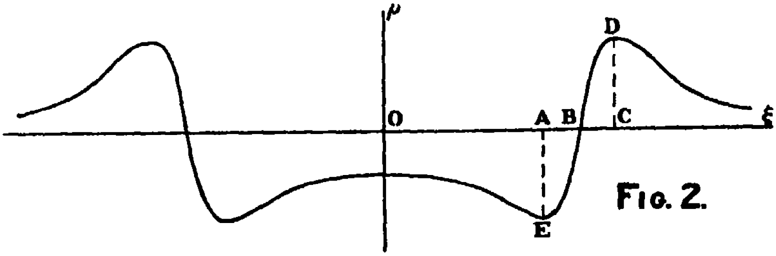

FIG. 2.

With different values of λ and μ, one could obtain variations in the relative prominence of OF compared with CD, and in other features.

If the roots of the denominator in (28) are $\pm(a \pm ib)$, we have

$$\left.\begin{aligned} 2(a^2 - b^2) &= \lambda^2 + \mu^2, \\ 2(a^2 + b^2)^2 &= \lambda^4 + \mu^4. \end{aligned}\right\} \tag{29}$$

Using these relations in evaluating the integral χ, we obtain

$$\chi = 2\pi i \left| \frac{2(\xi^2 - a^2 + b^2)e^{i\kappa\xi}}{\{\xi - (a - ib)\}\{\xi + (a + ib)\}\{\xi + (a - ib)\}} \right|_{a+ib}$$
$$+ 2\pi i \left| \frac{2(\xi^2 - a^2 + b^2)}{\{\xi - (a + ib)\}\{\xi - (a - ib)\}\{\xi + (a + ib)\}} \right|_{-a+ib}.$$

On simplification this leads to

$$\chi = 2\pi e^{-b\kappa}(b\cos\kappa a - a\sin\kappa a)/(a^2+b^2).$$

Hence from (7) the corresponding resistance is given by

$$(a^2+b^2)g\rho\mathrm{R} = 4\pi^2\kappa^2 e^{-2l\kappa}\sin^2(\kappa a-\epsilon), \tag{30}$$

with

$$\tan\epsilon = b/a.$$

We have in (30) a form very similar to those we have already studied. The phase ϵ means a bodily displacement of the series of humps and hollows; but, again, ϵ is small under the usual circumstances, when the difference between μ and λ is small compared with either.

Further, because of the symmetry of the distribution fore and aft, there are values of κ, with corresponding speeds, for which R is zero; we have seen that to avoid this result we must suppose the magnitude of the pressure p to be less in the vicinity of the run than at the entrance. We could introduce this want of symmetry by considering

$$p = \frac{\xi^2-c^2}{\{(\xi-a_1)^2+b_1^2\}\,\{(\xi-a_2)^2+b_2^2\}} \tag{31}$$

In the expression for the integral χ we should have a part corresponding to each of the poles a_1+ib_1 and a_2+ib_2; in consequence, the resistance R would be similar in form to the expression in (23).

From (30) we notice that the wave-lengths corresponding to humps on the resistance curve are submultiples of $2a$; also when λ and μ are nearly equal, $2a$ is of the order 2μ, the distance between the two positive pressure humps. The typical interference effects in this example are due to the interference of the bow and stern systems; in order to get a secondary interference effect between the positive and negative parts at the bow these must have separate individuality to a greater degree, as we saw in § 5. For instance, we could consider two distributions like (20), one associated with the entrance, the other reversed and associated with the run; we should then have a very general type of distribution represented by

$$p = \frac{\mathrm{A}_1(\xi-\frac{1}{2}l)}{(\xi-\frac{1}{2}l)^4-\beta_1(\xi-\frac{1}{2}l)+4\alpha_1^4} - \frac{\mathrm{A}_2(\xi+\frac{1}{2}l)}{(\xi+\frac{1}{2}l)^4+\beta_2(\xi+\frac{1}{2}l)+4\alpha_2^4}. \tag{32}$$

It is unnecessary to graph this or to put down expressions for χ and R. We should obtain a sum of expressions like (23) involving sines and cosines of $2\kappa a_1$ and of $2\kappa a_2$, and, in addition, of κl. There would be in general various possibilities of subsidiary interference effects; the main one would be the bow and stern interference represented by κl, and the next in importance that between the positive and negative parts at the bow represented by $2\kappa a_1$. There would also be the possibility of these two effects adding together at certain speeds.

9. One could obtain more maxima, or increased waviness, in the pressure curve by introducing higher powers of ξ into the fractions we have used. With the same general method for evaluating the integral χ it follows that we should obtain expressions of the same type, only more complicated in form.

The various examples which have been studied cover a wide range of distributions of the type which one would expect to be associated with the motion of a ship, in respect to the formation of transverse waves. It may be said that the corresponding resistance curves do not differ essentially from those obtained from a simple distribution, only with the introduction of additional coefficients there is possible a wider range of variation.

Attempts to Observe the Production of Neon or Helium by Electric Discharge.

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(Received and read December 11, 1913.)

§ 1. *Introduction.*

Very general interest has been aroused by the observations of Collie and Patterson on the above subject.[*] It is understood that their results have been endorsed by Sir W. Ramsay from independent evidence.

The present experiments were begun in the hope of confirming the work of Collie and Patterson and of sharing in the interesting field of research thus opened up. The results, however, have been negative, whether from a failure to appreciate the proper conditions for the production of neon or from some other cause.

There is no difficulty whatever in detecting helium or neon when isolated in approximate purity, and that the authors cited can have been deceived in the identification of these substances may safely be declared impossible. The only real doubt is as to where the neon or helium came from.

Very small quantities of air contain enough neon for spectroscopic detection. Some years ago I found[†] that 1/10 c.c. was enough. Rutherford and Royds[‡] afterwards succeeded with 1/15 c.c. of air, and in the present paper it will be shown that the neon spectrum can be well seen even in 1/100 c.c. of air. It is clear, therefore, that before anything can be inferred from the appearance of this spectrum, attention must be concentrated on the possibilities of atmospheric contamination.

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[*] 'Trans. Chem. Soc.,' 1913, vol. 103, p. 419, and 'Proc. Chem. Soc.,' 1913, vol. 29, p. 217.

[†] 'Roy. Soc. Proc.,' 1908, A, vol. 80, p. 593.

[‡] 'Phil. Mag.,' 1908, vol. 16, p. 813.

The helium spectrum may also be thus brought in, but only subordinately to the neon spectrum. If a helium spectrum is obtained practically free from neon it must be attributed to some other source than the atmosphere.*

If gas analysis apparatus such as a gas burette or a pump is employed, which has previously been used for manipulating large quantities of helium or neon, there must always be a risk that traces of the gas cling to it. It is essential to empty all such apparatus of mercury and to wash it out well with air. The mercury used should be either redistilled or well cleansed by bubbling air through it for a prolonged period and filtering. Without such precautions it is difficult to be sure that no trace of helium is entangled or dissolved in the mercury. These considerations have probably occurred to the authors cited, but they do not make any explicit mention of them.

Before neon or helium can be isolated by the use of charcoal it is essential to get rid of hydrogen from the gases, for hydrogen is not absorbed by charcoal with the necessary completeness. The procedure adopted by Collie and Patterson is to pump out the gases into a tube standing over mercury, and then to remove hydrogen by explosion with oxygen in a gas burette. My own preliminary experiments were also made in this way, and traces of neon were found in the gases, but I was never able to feel that the process of removing tubes from one trough to another, standing in a cup of mercury, could be carried out with satisfactory certainty of avoiding the entrance of minute air bubbles entangled between mercury and glass. The same may be said of pneumatic trough manipulation generally.

It must be admitted that the numerous blank experiments recorded by Collie and Patterson would seem logically to exclude the possibility of this having happened in their work. But, for my own part, I felt that the labour of carrying out such blank experiments would be very great, while preliminary experiments seemed to make it doubtful whether I should be able to attain complete freedom from atmospheric contamination. In any case, to achieve certainty a large number of positive results, alternating with blank experiments definitely and invariably negative, would be needed.

For these reasons a method was used by which hydrogen could be removed, and the test for neon carried out, without pumping the gas out of the apparatus or manipulating it over a pneumatic trough in any way. Special importance is attached to this feature.

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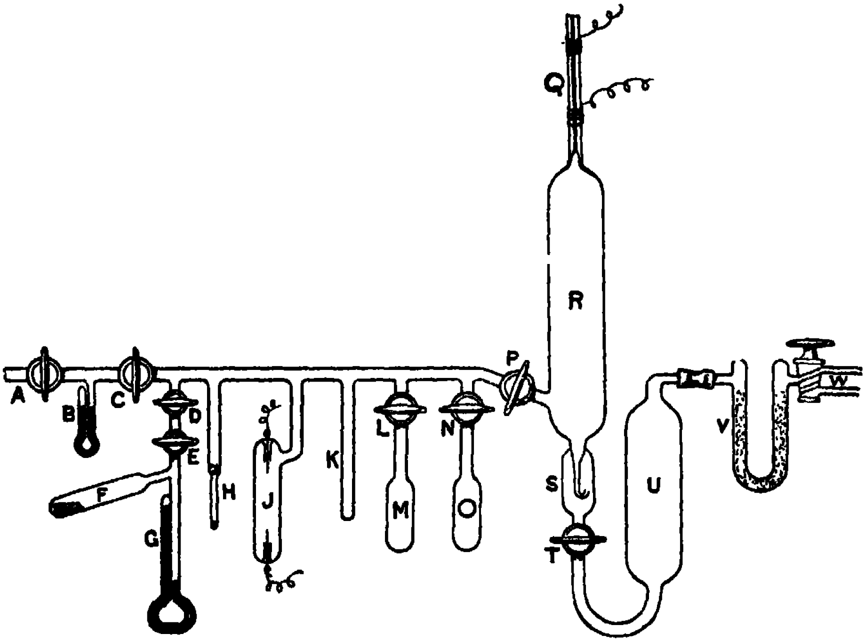
* A helium spectrum free from neon might no doubt be obtained by systematically fractionating a large quantity of atmospheric neon by cooled charcoal. In the text I assume one or two absorptions carried out with a minute quantity of gas at a very low pressure, as in the procedure described below.

§ 2. *Method of Experimenting.*

At the beginning of an experiment, all parts of the apparatus (see figure) were thoroughly exhausted through A by a Gaede pump. The charcoal condensers M, O, and the vessel R were well heated while the exhaustion was in progress. D, E, L, N and P were then closed and the pump finally shut off by means of the two stopcocks A and C. The space between them was thus left vacuous, and the small gauge B showed that it remained so. Thus C was not exposed to any but a very small pressure difference, and the chance of leakage from outside was minimised.



Hydrogen was generated in F by heating a piece of sodium about the size of a hazel nut which was contained in it.* Hydrogen thus generated is not open to the suspicion of containing air. The gauge G served to show the hydrogen pressure, and the space between the stopcocks, DE, to measure out small doses of it into the apparatus.

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* This method of generating hydrogen is very convenient in such cases. The sodium used is *dry*, *i.e.* it has never been placed in oil. Sodium in moderate sized pieces keeps quite well in a dry bottle, and the custom of defiling it with oil, generally prevalent in laboratories, has little to recommend it. A piece of sodium, coated with hydroxide from exposure to the air, allows of a vacuum being made over it when cold. When heat is applied hydrogen is given off; this is derived partly from chemical action of the sodium on the hydroxide, partly from gas occluded in the metal.

The discharge tube was varied from one experiment to another, but is indicated diagrammatically at J. The annexe K was kept cooled in liquid air, and served to keep the discharge vessel free from mercury vapour and carbon compounds. When the discharge had been kept on for the appointed time, a little oxygen was admitted to the apparatus, by heating the tube H, which contained a few milligrammes of potassium permanganate. The coil discharge was passed intermittently, for a few seconds at a time, and caused oxidation of the hydrogen present. At these low pressures the resulting water vapour quickly found its way by diffusion to the cooled tube K, where it was condensed. In this way, by passing the discharge a few times with one-minute intervals for diffusion, the hydrogen in all parts of the apparatus was quickly got rid of, the tube showing little or nothing but an oxygen spectrum.

The stopcock P was then opened, admitting the gases to R. The charcoal condenser M was first cooled, and the absorption allowed to proceed for about an hour. It was found advisable to heat the tube R again at this stage. M was shut off, and the second charcoal condenser O brought into action for an hour. P was then closed, and mercury run into R by opening T. The air trap S prevented any air bubbles being carried with it. The residual gas, which should contain helium or neon if any were present, was compressed into the very narrow tube Q, made of the finest thermometer tubing, where it could be measured or examined spectroscopically. The end of Q was not closed by fusion, but with a thread of sealing wax, which cut it off approximately square. The discharge could be passed by means of wires twisted on outside the tube, which were connected with an induction coil. They produced a discharge by electrostatic induction adequate to admit of spectroscopic examination, using the tube itself as slit. When the gas was first compressed into this tube, and the current passed, the pressure diminished, owing to chemical absorption of the gas, either by the glass or mercury. If no neon or helium were present, then, after a minute or so of discharge, further admission of mercury, by opening the regulating tap T, caused it to fill the capillary completely, leaving no interval visible, even with a magnifier, between the mercury and the sealing wax stopping at the top of the tube. The pressure at the top of the column was about one-third of the atmospheric, and the diameter of Q 0·169 mm. The minimum volume detectable may be taken as 7×10^{-7} c.c., which occupies 0·1 mm. length of Q when the mercury is let up.

If neon or helium were present, their spectra rapidly developed and attained purity as the discharge passed, and on finally opening T, the mercury did not rise to the top of the tube, but was separated from it by a measurable interval. Quantities, however, which were too small to occupy a measurable volume could still be detected spectroscopically.

Finally, it remains to be mentioned that the mercury was admitted to R from the vessel U, and could be sucked out again by a water pump attached to the three-way tap W. A calcium chloride tube V ensured that the air used to manipulate the mercury should be fairly dry.

§ 3. *Sensitiveness of the Test for Neon.*

The method of examining this was to admit measured volumes of atmospheric air,[*] to absorb with charcoal, and compress into the spectrum tube as described.

(1) With ½ c.c. of air, the neon spectrum was very brilliant indeed. When the mercury was allowed to run up, the length of gas column in capillary was 2 mm.

(2) With 1/10 c.c. of air, the neon spectrum was still very brilliant. Length of gas column ½ mm.

(3) 1/50 c.c. air. The yellow neon line was conspicuous even when the gas column occupied the whole length of the capillary tube. On compressing it to a length of 1 or 2 mm., the brilliant orange neon glow was seen, and a multitude of the red neon lines. In this latter case only one electrode of the coil was used, the other being earthed. Enough discharge was thus obtained. The gas volume when the mercury was let right up (one-third atmospheric pressure) was too small to measure; there was no interval visible, even with a magnifier, between the mercury column and the sealing wax plug which closed the tube.

From these experiments, it will be amply within the mark to say that the neon in 1/100 c.c. of air can be detected. I believe 1/1000 c.c. is nearer the true limit.

§ 4. *Description of Some Typical Experiments.*

In work of this kind, the technique is always modified and improved as the experiments go on. Nothing would be gained by describing the less satisfactory experiments—less satisfactory not because they gave any different result, but either from their short duration, from the impurity of the hydrogen spectrum in the discharge, or from the test for helium or neon not being carried out under the best conditions.

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[*] I have not thought it necessary to describe the additions to the apparatus required for doing this.

I pass over also a few experiments in which the gas was manipulated outside the apparatus. As mentioned already I have not been successful in excluding traces of air, amounting say to 1/50 c.c. or more, under these conditions.

Only one of the experiments made without transferring the gas gave *primâ facie* a positive result. This was with the electrodeless discharge. Hydrogen was admitted to the extent of about 0·5 c.c., to make up for absorption in the course of about 10 hours' run. The yellow neon line was observed, but not the red lines. The quantity of neon was probably less than that contained in 1/100 c.c. of air. The hydrogen used in this experiment was made by the action of dilute sulphuric acid upon zinc, and had stood over the acid, which was in contact with air, for some days. It is believed that the hydrogen was contaminated with air which had diffused through the liquid, to the extent of say 1 per cent., which would explain the result. When the experiment was repeated with hydrogen which was above suspicion, no neon could ever be detected.

I pass therefore to the description of the final experiments, on which reliance is chiefly placed.

Experiment 1.—A cylindrical discharge tube* of about 9 cm. length and 2 cm. diameter, provided with aluminium wire electrodes, was exhausted, and run long enough to get most of the gas out of the electrodes. Finally it was charged with hydrogen at such a pressure as to give a striated discharge without much cathode phosphorescence. About 0·1 c.c. of hydrogen was admitted for this purpose. A large induction coil with mercury interrupter was used, and a current of 2 to 3 ampères was passed through the primary circuit. This made the tube as hot as was judged safe. The pressure slightly increased during the experiment, which was continued for eight hours. The residue in this, as in all the following experiments, shrank sensibly to nothing, *i.e.* it occupied a length certainly less than 0·1 mm. in the capillary tube. The volume of gas, reduced to atmospheric pressure, was certainly less than 7×10^{-7} c.c. No neon or helium were seen spectroscopically Mercury lines were the only ones visible. The volume test for neon is much less sensitive than the spectroscopic and is valuable only as showing that no foreign gas is present to mask the neon spectrum.

Experiment 2.—The same tube was run for five hours at low pressure, showing cathode ray phosphorescence (5 to 10 mm. alternative spark-gap). After that the pressure rose somewhat, owing to liberation of hydrogen during an additional run of three hours. Residual gas occupied 0·0 mm. length in capillary tube as before. Primary current 2 to 3 ampères; no neon or helium by spectroscopic observation.

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* The tube used in this experiment is the one shown in the figure. It was replaced by other forms as occasion required.

Experiment 3.—A spherical bulb of soda glass, 100 c.c. capacity, was attached to the apparatus. A coil of 6 turns of insulated wire was placed over it, and an electrodeless discharge maintained by constantly discharging a large leyden jar through the coil, with a spark-gap in series. The jar was charged with the induction coil previously mentioned, passing 4 to 5 ampères through the primary. This was as much as the coil would bear for long runs, as larger currents made it dangerously hot. The discharge in the bulb was bright red, and concentrated in a well defined ring. Absorption of hydrogen began as soon as the discharge was started. It was most marked when the bulb was new, but continued, though less energetically, throughout.

The amount of hydrogen necessary to be admitted during a day's run, to keep the conditions constant, was usually about 0·25 c.c. The first day, the discharge was run 10 hours. Length occupied in capillary tube, 0·0 mm. No neon or helium in spectrum. The (invisible) residue from this run was kept in the capillary spectrum tube, and more hydrogen introduced into the discharge bulb. Next day 9 hours' run was given. The total hydrogen admitted in the two days was about 0·5 c.c. The united residue from the two runs was examined. Length of capillary occupied, 0·0 mm. The spectrum showed no trace of helium or neon.

[Experiment 4.—A Plücker spectrum tube was used with copper wire electrodes. The capillary was 9 cm. long and 1 mm. diameter, and the terminal enlargements each 7 × 1·3 cm. Hydrogen was admitted to a pressure a little above that of cathode phosphorescence, and a strong discharge passed. Absorption of gas was rapid, particularly at first, and the tube repeatedly ran "hard" and required replenishing. Thus the discharge passed under a variety of conditions as regards pressure. A bulb of 100 c.c. capacity was in connection with the tube, so as to make the pressure variations less rapid. Total run, 13 hours. Residue, 0·0 mm. length in capillary tube. No neon or helium visible in spectrum.—*January*, 1914.]

Experiment 5.—The tube used in this experiment was designed for bombardment of solids by cathode rays. It was charged with potassium chloride, using a considerable mass of the salt, to protect the glass from bombardment. The salt was heated before introducing it, and under these conditions the vacuum was maintained without pumping during the bombardment. Any water or carbon dioxide given off was condensed in the annexe cooled in liquid air, used in this as in all the experiments.

Primary current, 2 to 3 ampères; 10 hours' run. The hardness of the cathode rays was indicated by an alternative spark-gap of 5 to 10 mm. The rays at first turned the salt blue, but more energetic and long continued bombardment decolorised it again. Length of capillary occupied by residue, 0·0 mm. No helium or neon seen in spectrum.

Experiment 6.—Similar to the preceding, except that potassium iodide was substituted for potassium chloride. Primary current, 1 ampère; 7 hours' run. Alternative spark-gap about 1 cm. Iodine was set free in the bombardment, and a deposit of it could be seen in the cooled tube. Length of capillary occupied by residue, 0·0 mm. No helium or neon in spectrum.

In this and the previous experiment, while the bombardment of the salt was in progress, the hydrogen spectrum could be seen in some parts of the tube, suggesting that most of the residual gas was hydrogen. These experiments are therefore relevant to the question of production of neon from hydrogen.

§ 5. *Conclusion.*

It will be seen, then, that these attempts to confirm Collie and Patterson's results have not met with any success. It may be that the authors will be able to point out wherein the essential conditions have not been complied with, and thus help the attainment of a successful result. In that case the present paper will have had its use, in eliciting further details from them.

The experiments on electrodeless discharge would seem to deserve special scrutiny. For this kind of discharge can only be obtained under a limited range of conditions; in this case the issue as to the cause of discrepancy would seem to be a good deal narrowed.

I feel confident that the present negative results are not due to any defect of the technique in looking for neon. Most rigorous precautions have to be taken to avoid getting this spectrum from atmospheric contamination.

The experiments (5, 6) on bombardment of potassium salts by cathode rays would have been expected, from Sir J. J. Thomson's results,[*] to have yielded evidence of helium. That they did not do so may be due to deficient sensitiveness of the spectroscopic as compared with the positive ray method of analysis. We have no very definite data as to the sensitiveness of the latter.

[*] 'Roy. Soc. Proc.,' 1913, A, vol. 89, p. 18.

The Positive Ions from Hot Metals.

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It is well known that when a metal wire or strip is heated for the first time there is a large emission of positive ions from it at a comparatively low temperature. This emission takes place even if the wire is carefully cleaned and the heating is carried out in a good vacuum. It decays to a small value under continuous heating in a vacuum, and can be revived to a varying extent by a number of different modes of treatment, such as heating in air, or in a bunsen flame, or by subjection to high pressure. Very different conclusions as to the nature of these ions have been reached by different experimenters. One view, which has, perhaps, had more advocates than any other, is that the ions consist of positively charged atoms or molecules of various gases evolved by the hot substances. For several years I have suspected that these ions would turn out to be atoms or molecules of the commoner alkali metals which are present in the heated metals as impurities. The experiments to be described were undertaken in the hope of deciding the question in a definite manner.

The direct and obvious way of attacking the problem is to determine the specific charge (e/m) of the carriers. Since the value of the corresponding quantity for the standard chemical element in electrolysis is known, this is equivalent to measuring the electric atomic (or equivalent) weight (m/H). I have already made experiments with a large number of metallic substances in this way, partly in collaboration with Mr. Hulbirt.* The results showed that the electric atomic weight of the ions was of the order of 30 for the 14 different substances tested, but the measurements were not sufficiently exact to determine with certainty whether the ions were atoms of sodium and potassium or molecules of some of the commoner gases, such as carbon monoxide. The electric equivalent weight of CO_+ is 28, and is thus intermediate between Na_+ (23·05) and K_+ (39·1). There are a number of other alternative constituents which suggest themselves.

The method of measurement was the same in principle as that used in the earlier experiments, but has been improved in a number of details, so as to ensure higher accuracy. The entire apparatus has been enlarged, so that the distance between the slit and the strip ranged around 1·35 cm. instead of

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* 'Phil. Mag.,' 1908, vol. 16, p. 740; 1910, vol. 20, p. 545.

0·45 cm., the other dimensions being made to correspond. The strips were cut 0·1 cm. wide with the dividing engine, and almost filled the slit in the brass plate in which they were placed, only about 0·01 cm. clearance being left on either side. As the formula for e/m contains the distance between the strip and the opposite slit raised to the fourth power, it is important that this distance should be perfectly definite and capable of precise measurement. An improved method of measuring this distance was employed. A low-power reading microscope, with its axis horizontal, was arranged to travel in a vertical direction. The axis of the microscope pointed lengthwise along the middle line of the strip and of the slit, which was vertically above the strip. The microscope was focussed on the point of a pin placed at the centre of the strip before measuring the distance between strip and slit. Thus the distance measured was that at the middle, but measurements made in other parts did not show any appreciable difference.

The greatest source of uncertainty in the earlier measurements, in all probability, is caused by the bowing of the heated strip due to thermal expansion. The change in the distance between the strip and the opposite slit which is produced in this way is rather variable, as it depends on the stiffness of the strip and the way in which it is attached to the end supports. It may, however, introduce quite serious errors into the final value of e/m. This difficulty was entirely overcome in the present experiments by mounting one of the platinum terminals, to which one of the ends of the strip was attached, on the free end of a strip of phosphor bronze several centimetres long and of suitable thickness. The heated metal strip was then at right angles to the phosphor bronze strip, which was arranged to keep it under a slight tension. The extent of the outward motion of the phosphor bronze spring was limited, and could be regulated, by a small screw. A good deal of difficulty was experienced at first in getting the amount of tension right. If the spring is too stiff it breaks the metal strip, which becomes quite soft at a high temperature; on the other hand, if it is too weak, it is not able to keep the heated strip taut. After some trials it was found that the proper amount of tension could be estimated without much difficulty.

The strip itself was soldered to platinum studs, one of which was attached to the phosphor bronze spring in the manner just described. The ends of the studs were the least bit below the surface of the plate, and the strip was pulled over them and bent round, and then soldered to the side of the studs. The tension of the spring caused a good electrical contact to be established between the strip and the ends of the studs, where there was no solder. In this way there was no danger of the solder getting on to the hot parts of the strip. The strips were accurately cut in the dividing engine, so as to be uniform in width, and were very carefully cleaned. In the case of platinum they were boiled in hydrofluoric acid, nitric acid, and distilled water in succession. When mounted they were flush with the brass plate. Both this plate and the opposite divided plate were ground flat and mounted so as to be parallel. The hard rubber blocks, to which the plates were formerly screwed, were discarded, and replaced by quartz tubes, accurately ground perpendicular to their axes, so as to be equal in length. The plates were held together by brass screws, which passed through holes in the plates and down the centre of the quartz tubes. The screws and nuts were insulated from the brass plates by hard rubber bushings. In this way changes in the distance, which might have been caused by the somewhat considerable and rather irregular expansion of the hard rubber, were eliminated. The micrometer screw which was used for measuring the displacement of the maxima was carefully checked up. It was found that the errors were too small to be worthy of consideration.

Many other changes have been made in the mechanical construction of this apparatus since the form figured in the 'Philosophical Magazine,' 1908, vol. 16, pp. 744, 747, was made. The construction of the tube has been altered, so that the plates lie in horizontal instead of vertical planes. There are now three leads corresponding to A and B (fig. 2, *loc. cit.*), one for the electrode behind the slit and the others for the two plates. Thus, either the slit or balance method* may be employed by simply changing the connections outside the tube. These leads are provided with brass springs, and are connected to the apparatus with platinum hooks and eyes. They pass out through a glass stopper. The whole of the micrometer screw, including the head and counting device, is now enclosed in the evacuated glass apparatus, thus eliminating the mercury column RQ_3. The screw is driven by means of a right-angled bevelled gear, which is turned by a ground glass stopper. The fractions of turns are read off on the micrometer head through the glass, and the whole turns on a cyclometer, also enclosed.

A good deal of attention was paid to the measurement of the magnetic field H. In the former experiments this was done by the change of resistance of a bismuth spiral. This method is not a very accurate one with magnetic fields of the strength used, and could not be employed when the measurements of e/m were actually being carried out. This introduces the chance of a further error, owing to possible changes in the temperature of the magnet, if, as was the case, the exciting current is used as an intermediate indicator of the magnetic field. The procedure adopted in these experiments was more complicated but more reliable. A marble block of square cross-section was wound with 20 turns of fine wire, so that all the induction was along the axis of the solenoid and was calculable. The terminal wires were carried back to the middle of the coil, so as to cancel the sideways induction, and then twisted together. This standard of induction was placed with its axis parallel to the magnetic field in the place between the poles of the electromagnet occupied by the paths of the moving ions in the measurements of e/m.

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* *Cf.* 'Phil. Mag.,' 1913, vol. 26, p. 452.

The cross-section of the solenoid was 1·407 cm.^{2}, so that the area of the field was comparable in the two cases. The solenoid was arranged in series with a sensitive fluxmeter, and the throw measured when the electromagnet was reversed. The fluxmeter was then placed in series with the secondary of a standard mutual inductance which was tested at the Bureau of Standards and found to be equal to 0·010175 henry. The throw of the fluxmeter was then determined, when a known current in the primary of the mutual inductance was reversed. This current was measured by comparing the fall of the potential, when it flowed through a Wolff standard resistance, with the electromotive force of a cadmium cell, which had been tested by Hulett, using a Wolff potentiometer. As a matter of fact the current in the primary was adjusted so that the current it induced would produce the same calculated throw in the fluxmeter as would be produced by a field of 3000 lines threading the standard marble inductance. The current exciting the magnet was then adjusted until the two throws, due to reversal, were exactly equal. In this way errors arising from the varying sensitiveness of different parts of the fluxmeter scale were eliminated. Before testing the effect of the magnet several preliminary reversals were carried out to get rid of effects due to hysteresis.

In this way the measurement of the magnetic field was made to depend upon a knowledge of the following quantities:—The calculated inductance of the solenoid, the standard of mutual inductance, the standard of resistance, and the electromotive force of the cadmium cell. These are all known with a high degree of precision, so that the limit of accuracy would appear to be set by the accuracy with which two equal deflections of the fluxmeter can be compared. The deflections were about 300 scale divisions, and an accuracy of 0·5 per cent. is probably a conservative estimate of what was attained. An attempt was made to reduce the comparison to a null method, but this was unsatisfactory on account of the difference in the time constants of the circuits compared. The insertion of such self inductances as were available did not mend matters very much, so that the adjustment to equality of deflections was adopted.

So far the above process is open to one of the objections to the bismuth spiral method, since it can be used only when the measurements of e/m are not being carried out. This difficulty was overcome by using as an intermediate standard a single circular turn of wire attached to the end of one of the pole pieces. The flux through this was checked up against that through the solenoid by means of the fluxmeter, and the throw from the single turn due to reversing the magnet could be compared with that from the mutual inductance at any time when the measurements of e/m were being made. As a matter of practice it was found that if the temperature of the magnet was kept constant the magnetic field due to a given exciting current remained the same, so that to keep the same magnetic field it was only necessary to watch the temperature of the magnet and the value of the exciting current as shown on a standard Weston ammeter. Separate tests showed that the flux across a square centimetre did not vary as much as 1 per cent. over the whole area of the flat ends of the pole pieces (40·7 sq. cm.). The magnetic fields used were thus very uniform.

The static potential difference between the strip and the opposite plates was always kept at exactly 200 volts. This was done by means of a battery giving rather over 200 volts in series with a variable opposing potential taken from a few cells in series by means of a sliding rheostat. The potential was adjusted to 200 volts by the potentiometer; 1,001,000 ohms was placed across the whole battery, and the drop on the 1000 ohms was compared with a standard electromotive force.

The measurements of e/m were made by a slight modification of the balancing method* described in one of my former papers.† This type of method has the great advantage that the immediate determination of e/m requires only two simple measurements which can be carried out in about a minute, so that the change of e/m with time can be followed even when it is altering rather rapidly. I have compared this method with the more laborious slit method under the improved conditions, and they agree absolutely, so far as I am able to tell. It is probable that the deviation from the theoretical formula observed in the older experiments† was due either to the theoretical conditions not having been satisfied or to an inaccurate knowledge of some of the data.

In the former measurements the value of e/m for the negative electrons was taken as a kind of absolute standard in determining e/m for the positive ions. This method possessed certain advantages when it was important to determine with some degree of reliability even approximate absolute values of e/m for the positive ions, but it cannot claim to be of value in determining the value of e/m for the positive ions with precision in the present stage of development of this method of experimenting. In fact the accuracy which has been attained in the measurement of e/m for the positive ions in this way is, so far, very much greater than that for the negative electrons. Very likely this is to a large extent simply a matter of insufficient experience, but there are difficulties, such as those conditioned by electron reflection, that arise in the case of the negative electrons which do not occur with the positive ions. At any rate, the measurements that were made with the negative electrons in the former apparatus led to quite irregular results, so that no use has been made of them in the present investigation. It is, however, desirable to have some check on the results which does not depend directly on the rather considerable number of measurements required in getting absolute values. This was furnished by placing potassium sulphate on the strips and measuring e/m for the positive ions from this substance. The writer has already shown that the positive ions from the salts of the alkali metals are univalent atoms of the constituent metal. The ions from potassium sulphate have a value of e/m which is indistinguishable from that of the majority of the ions given by the metals tested, so that this substance is extremely well adapted for checking the values otherwise obtained.

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* See also 'Phil. Mag.,' 1913, vol. 26, p. 452.

† 'Phil. Mag.,' 1908, vol. 16, p. 740.

It is worth while pointing out that in the old experiments in which the value of e/m for the electrons is made use of, the results are over-corrected in any event, as the value e/m ($1{\cdot}88 \times 10^7$) which was taken as the standard is about 6 per cent. higher than that which is now accepted. Moreover, the correction for the lack of uniformity of the electrostatic field which is discussed in the 'Philosophical Magazine,' 1908, vol. 16, p. 763, must now be very small, as the clearance between the strip and the surrounding plate (0·01 cm.) was only about one-tenth of the width of the strip. It is rather significant that the values of e/m do tend to run about 2 per cent. lower than what seems to the writer to be the most probable value.

Results of the Experiments.

The substances which have been tested with the improved apparatus and method are platinum, potassium sulphate, manganin and iron. The number of different kinds of metal strips which can be subjected to a sufficiently extensive examination in this way is rather limited, as there are not many which will stand the required tension at high temperatures. The strips were carefully cleaned before mounting. The part which was subsequently heated was never touched except with platinum tweezers, and the greatest care was taken to avoid any possible contamination of this part of the strip with possible impurities. The heating current was regulated so that the thermionic current was kept at a suitable value to make measurements with. This involved a gradual increase in the temperature of the strip as the heating progressed, on account of the decay of the emission with time. The pressure of the external gas was less than 0·001 mm. on the McLeod gauge, except in certain special experiments. The temperature of the strip was obtained from its resistance, although it is only a matter of secondary importance.

The results obtained are expressed in terms of the electric atomic weight m/m_1 of the ions, which are supposed to be univalent, instead of e/m. The values of m/m_1 are obtained by dividing the value of e/m for a univalent electrolytic ion of unit atomic weight, which is 9649 E.M.U., by the measured values of e/m. This enables a direct comparison with the chemical atomic weights (in terms of $O = 16$) to be effected. The values of e/m were obtained by substituting the experimental numbers in the formula

$$e/m = \frac{9}{2}\frac{Vx^2}{H^2z^4},$$

where V is the electrostatic potential difference between the opposite plates, H is the intensity of the magnetic field, x is half the displacement of the balance which occurs when the field is reversed, and z is the distance between the front of the strip and the front of the opposite plates. V was always 2×10^{10} E.M.U., and H was always 3000 E.M.U., $2x$ was comparable with 0·5 cm., and z with 1·35 cm.

As an illustration of the uniformity of the results given by this method under favourable conditions the numbers given by one of the preliminary tests may be cited. A strip which was clean in appearance, but which had not been specially cleaned, was heated for several hours and then kept under fairly continuous observation for a period of five hours longer.

During this time 16 determinations of m/m_1 were made and all of them lay between 39·75 and 40·2. In general the uniformity is not so high as this, although deviations in excess of 3 per cent. of m/m_1 are very rare. A good deal seems to depend on whether the strip is comfortable or not. A minute twisting or displacement of the strip in between two readings will cause a serious deviation. The position of the balance can easily be determined to one-hundredth of a turn (0·000635 cm.). This means about 0·1 per cent. of $2x$.

Another preliminary test gave the following values of m/m_1. The length of time the strip had been heated and the instantaneous platinum resistance temperatures are also given.

Time (minutes) ...	0	10	15	25	30	35	45	55	70	85
Temp. (° Pt)	468	468	468	492	492	492	492	492	508	508
m/m_1...............	40·6	40·7	40·8	40·2	40·4	40·7	40·6	40·6	40·1	40·3
Time (minutes) ...	100	105	125	150	170	190	195	205	210	285
Temp. (° Pt)	525	525	525	525	525	535	535	535	535	668
m/m_1..................	39·9	39·9	39·8	39·9	39·8	39·8	39·3	40·1	39·1	39·9
Time (minutes) ...	300	310	320	330	345	350*	360	370	380	385
Temp. (° Pt)	668	668	668	690	690	690*	480	514	514	525
m/m_1............... .	39·3	39·5	39·8	39·8	39·9	40·6*	39·7	39·7	42·9	41·1
Time (minutes) ...	390	395	480	520						
Temp. (° Pt)	525	525	579	614						
m/m_1..................	41·6	41·0	40·4	39·6						

The strip broke at this stage. At the point indicated thus* it was found to be behaving unsatisfactorily. The strip was cooled and the apparatus taken down, when it was found that the strip had warped and come into contact with one side of the slit in the brass plate. The subsequent measurements were taken after the strip had been readjusted and the apparatus set up again.

It is clear that there is no definite indication of any change in the electric atomic weight of the ions given off by the above strip in the space of 8 hours 40 minutes during which it was heated. The mean value of the electric atomic weight is very close to 40. The breaking of the strip is to be attributed to the combined effect of the tension of the spring and the high temperature. The resistance of the strip only gives the average temperature, and no doubt the central portions were much hotter than the recorded temperatures indicate.

In order to find out if long continued heating would change the nature of the ions another carefully cleaned strip was taken and heated for 36 hours under + 200 volts, but without any tension. This was accomplished by means of the limiting screw already referred to. The screw was then turned back so that the spring would pull the hot strip taut. Three measurements extending over 25 minutes were then made before the strip broke. They gave the following values of m/m_1 in succession: 25·1, 25·3, 24·2. Thus after the positive ionisation from platinum has been allowed to decay for a long time it is found that the ions have a much smaller atomic weight than those which are first emitted.

After some experimenting it was found possible so to adjust the tension of the spring that not only both the stages referred to but also indications of a third kind of ions could be demonstrated on the same strip. Some of the values given by the most satisfactory experiment of this kind are indicated thus: ×, in fig. 1. Some of the numbers in the table above are also plotted thus: ◀ for comparison. The figure also contains some of the data given by a test made on potassium sulphate. In this experiment a strip was glowed out until it had lost the power of emitting positive ions except at a very high temperature, and then a small quantity of a solution of pure potassium sulphate in distilled water was placed on it. In making the measurements the strip was stretched by the spring as in the other cases. In fact the clean platinum strip was glowed out until the emission at 1011° Pt was too small to make measurements with. When the strip was cold the apparatus was taken down and the solution of K_2SO_4 sprayed on to it in such a manner that none of the spray got on to any part of the apparatus except the front surface of the strip. It was then found that the emission at 320° Pt was plenty large enough to work with. All the measurements which were made in this experiment are collected in the following table:—

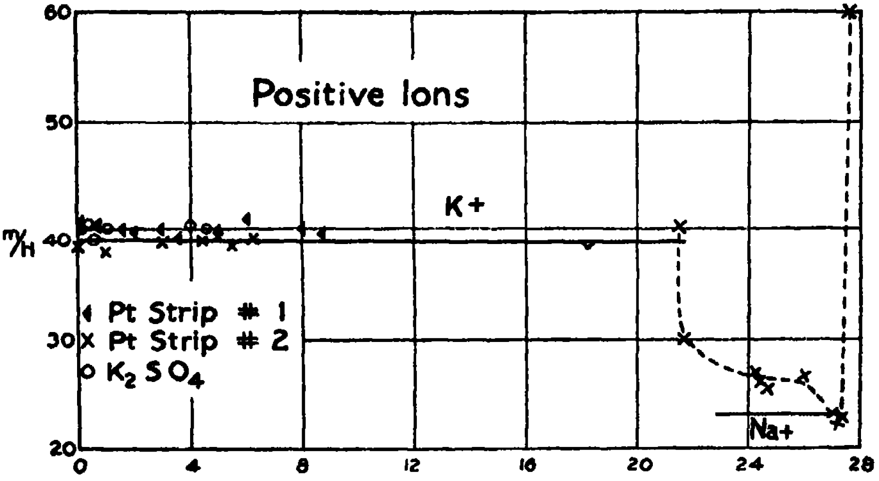

FIG. 1.

Time heated (minutes)	0	10	17	25	30	40	50	60	235	275	280
Temperature	320	320	330	330	330	330	330	350	350	500	500
m/m_1	40·4	40·6	41·1	40·7	39·2	39·7	40·1	40·2	40·3	41·6?	39·8

Mean = 40 2.

Only a few of these values of m/m_1 for the ions from potassium sulphate are plotted in the figure. They are indicated thus: ○. The current which was flowing from the hot strip during the experiments recorded in this paper was not maintained constant. It was, however, kept at a value which was convenient to work with, and was thus always comparable with 0·01 electrostatic unit.

Returning to fig. 1 the horizontal line on the left represents the chemical value of m/m_1 for the monovalent ion K_+, and the horizontal line to the right the corresponding value for Na_+. The points marked thus: ×, do not represent the whole history of the ions from strip No. 2. This strip was heated for about 14 hours before commencing observations, in order to drive off most of the initial ionisation. Numerous independent experiments have amply shown that this initial ionisation is made up entirely of ions for which m/m_1 is equal to about 40, so that we may conclude that during the first 36 hours of heating under these conditions practically all of the positive ions emitted are of the same character. Although the experimental value of m/m_1 for them runs a little higher than the chemical value for K_+, there is no demonstrable difference in the numbers given by them and those given by the ions from K_2SO_4. As there are good reasons for believing the latter to be atoms of potassium which have lost an electron, there does not, so far, seem to be any reason for doubting the identity of the ions in the two cases. Alternative possibilities will be considered later.

Although the data are not at all precise, it is worth while to estimate the amount of matter which is emitted in the form of these positive ions. In the above experiment in which the strip was under observation until all the ions for which m/m_1 is in the neighbourhood of 40 had been emitted, the current during the 14 hours of preliminary heating was greater than afterwards. Allowing a factor of about 2·5 for this, I find that the total quantity of electricity carried away in the form of these ions would be 10^{-6} coulomb or 10^{-7} E.M.U. Putting $e/m = 246{\cdot}5$ (the value for K_+) the mass of matter carried away in this form $= 4{\cdot}05 \times 10^{-10}$ grm. If an equal amount escapes from the back of the strip the total would be $8{\cdot}1 \times 10^{-10}$ grm. The mass of the heated part of the strip was approximately $5{\cdot}5 \times 10^{-2}$ grm. Thus the proportion of the matter present which is emitted in the form of these positive ions is about $1{\cdot}5 \times 10^{-8}$, or $1{\cdot}5 \times 10^{-6}$ per cent. Some data given by Horton* for an experiment made at a much higher average temperature (1190° C.) lead to a rather similar estimate. The similarity of these two estimates rather points to the view that the quantity of electricity emitted in the form of these ions does not depend much on the temperature of emission. The simplest explanation of this result would be that practically all of the available matter is expelled in the ionised form. If that is the case the total amount of matter concerned is so small that its detection by chemical methods is not very hopeful. This question cannot be regarded as definitely settled by the data now available, as the dependence of the total amount of matter emitted in the form of a given kind of ions upon the method of heating requires further examination.

* 'Roy. Soc. Proc.,' 1913, A, vol. 88, p. 135.

Turning again to fig. 1 we see that after about 36 hours of heating (22 on the diagram) there is a rather sharp drop in the value of m/m_1, after which values in the neighbourhood of Na_+ are approached somewhat gradually. In this region the values obtained are apt to be irregular and point to the occurrence of a mixture of ions. It may be that the values in the neighbourhood of 26 correspond to something definite, but the irregularity of the results usually obtained when the average value is in this neighbourhood do not lend support to such a view. Until further evidence appears it seems most reasonable to suppose that in this neighbourhood we are dealing with a mixture of Na_+ and K_+. With platinum strips the sodium values only occur at a high temperature and after continued heating. They never last very long, so far as I have been able to observe.

With the strip under consideration the last value, which was obtained very shortly before the strip broke, is very close to 60. With very old strips I have frequently observed the presence of ions for which m/m_1 lies between 50 and 60. I am inclined to attribute them to the presence of Fe_+ (56) Unfortunately they do not last very long, and the behaviour at this stage is rather irregular, so that it has not been possible to get really accurate results. I have often looked for heavy ions such as Pt_+ ($m/m_1 = 195$) from strips which have been subjected to long continued heating, but I have never been able to observe anything of the kind.

After making several unsuccessful attempts with gold strips, which always broke under the tension required to keep them straight, before a sufficiently large or permanent ionisation to make measurements with could be obtained, strips of manganin were tried. These were rolled from resistance wire to the requisite width and thinness, and were cleaned in ether, dilute nitric acid, and distilled water before being mounted. The initial heating current was 0·65 ampère, and this had to be raised gradually to 0·84 ampère as the heating progressed, owing to the decay of the emission. No attempt was made to estimate the temperature, but it was not very different from that of platinum when heated for the same length of time. A series of measurements of m/m_1 which were extended fairly evenly over a period of four hours gave the following successive numbers:—39·3, 39·7, 39·4, 41·0, 40·2, 39·3, 39·7, 39·5, 39·7, 40·0, 41·4, 40·8, 40·0; mean 40·0. Thus the positive ions given off by manganin have the same electric atomic weight as the bulk of those given off by platinum, and there seems to be no valid reason against referring them to the same ingredient.

Two different specimens of iron wire were tested in the same way. Both of them were said to be especially pure iron, but they were not analysed. The wires were rolled into strip and washed with ether, dilute hydrochloric acid, and distilled water, before mounting. The specimen from the first sample had a resistance of 174 arbitrary units at 40° C. Only four observations were made on this specimen. The times, resistances, and values of m/m_1 were as follows :—

Time heated (minutes)	10	25	46	55	
Resistance (arbitrary units)	524	524	504	504	
m/m_1	39·9	39·9	39·8	40·0	Mean = 39·9.

Two specimens from the second sample were tested. The first gave the following numbers :—

Time heated (minutes)	0	?	39	?	?	75	80	95	105
m/m_1	24·2	37·1	37·8	33·3	39·9	42·6	40·7	46·0	73·5

Thus the first specimen gave no indication of anything except the ions which have been attributed to potassium, and the second gave rather similar values over most of the corresponding time. In addition, the second specimen gave indications of something with a lower value of m/m_1, which, may have been Na_+ (23·05) at first, and also considerably higher values, 46 and 73·5, just before the strip broke. These are well above the potassium value, and may be taken to indicate Fe_+ (56). The last high value is a little uncertain, as the strip broke before the observation could be repeated, but there is no doubt that values much higher than 40 were being got at this stage. Another specimen from this second sample was tested. Unfortunately, both the initial and final stages were missed owing to the occurrence of accidents. The results, however, are of interest, as confirming the conclusion drawn from the other tests, that the bulk of the ions from iron have the same value of m/m_1 as those from platinum and manganin. The data given by this specimen are as follows :—

Time observed (minutes)	0	10	30	60	90	180	195	215	225	255	315
Resistance (arbitrary units)	1084	1084	1144	1244	1314	1594	1594	1614	1694	1804	1894
m/m_1	38·3	39·5	40·0	40·0	39·9	42·1	40·5	40·5	39·7	39·4	40·9

Mean m/m_1 = 40·1.

The resistance at 40° C. was 334 in the same units.

I have already mentioned that the view that the positive ions from freshly heated metals consist of charged atoms or molecules of one or more of the commoner gases, such as carbon monoxide, hydrogen, carbon dioxide, nitrogen or oxygen, has obtained a considerable number of adherents. As the respective electric molecular weights of the ions which might be expected to arise from these gases are the following: $CO_+ = 28$, $H_+ = 1$, $H_{2+} = 2$, $CO_{2+} = 44$, $N_+ = 14$, $N_{2+} = 28$, $O_+ = 16$, and $O_{2+} = 32$, it will probably be conceded that the present experiments do not lend any support to such a view. The only common gas for which the value of m/m_1

is near enough to the measured values is argon ($Ar_+ = 39{\cdot}9$). The value for argon would, in fact, fit the experimental results better than that for potassium, but there are other reasons, which will be considered below, which seem to the writer to make potassium the more probable constituent. It would, of course, be a matter of very great interest if it could be established that these ions are charged atoms of argon.

Let us review very briefly some of the more important experimental results which tend to support the view that these ions are charged atoms or molecules of one or more of the commoner gases. Most of these will be found enumerated in the following list:—

(1) A platinum wire, which has lost the power of emitting positive ions owing to continued heating in a vacuum, is found to regain this property to a considerable extent if it is re-heated (*a*) in air at atmospheric pressure, and especially (*b*) if it is heated in a bunsen flame.*

(2) A similar recovery takes place when the wires are exposed to various gases under a pressure of 50 to 100 atmospheres at a relatively low temperature† (about 200° C.).

(3) When most metals are heated there is a considerable evolution of gas, the bulk of which usually consists of hydrogen, carbon monoxide, and nitrogen.

(4) When a wire has been heated for a long time so that the emission in a vacuum has become too small to measure, there is an emission in different gases, which seems to be a definite function of the nature and pressure of the gas. This phenomenon has been most completely studied in the case of platinum in an atmosphere of oxygen.‡ The facts have been explained by the writer on the hypothesis that the metal absorbs or adsorbs the gas, which it re-emits in the form of charged atoms. It has been suggested by various writers that the initial emission is an intensification of this phenomenon, owing to the presence of much larger amounts of absorbed gas in the original metal.

(5) Horton§ has found that carbon monoxide has a greater power of stimulating the emission of positive ions both from hot platinum and from heated salts than the other common gases, with the exception of hydrogen.

(6) Determinations by Garrett‖ of e/m for the positive ions given out by aluminium phosphate when heated led him to conclude that these were atoms of hydrogen.

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* *Cf.* Horton, 'Roy. Soc. Proc.,' 1912, A, vol. 88, p. 131.

† Z. Klemensiewicz, 'Ann. der Phys.,' 1911, vol. 36, p. 796.

‡ O. W. Richardson, 'Phil. Trans.,' 1906, A, vol. 207, p. 1.

§ Horton, 'Camb. Phil. Soc. Proc.,' 1911, vol. 16, p. 89.

‖ Garrett, 'Phil. Mag.,' 1910, VI, vol. 20, p. 582.

We shall now consider how the facts just enumerated can be reconciled with the results of the measurements of m/m_1 which have been described. In the absence of definite information, the obvious explanation of (1) (*a*) and (1)′(*b*) seemed to be that the revived ionisation was due to a different cause from the ionisation from the fresh wire; that the initial ionisation might be due to the impurities in the wires, which have been tentatively attributed to potassium, whereas the revived effect might be due to the re-emission of absorbed gas, air in the case of (*a*), and gases from the bunsen flame in the case of (*b*). This view can readily be subjected to the test of experiment, for, if it is correct, the ions from the revived wire should have a value of m/m_1 different from that of those from the fresh wire. The tests were carried out with the platinum strips, and the effect of heating in dry filtered air at atmospheric pressure was tried first. The strip was glowed out until there was no measurable emission at about 700° Pt. It was then heated in air in the apparatus with the strip loose. This heating was carried out during a succession of short intervals with longer cold intervals between, the object being to prevent the whole apparatus from getting heated. After the strip had been heated in air at a high temperature for about 10 minutes altogether, the apparatus was taken down, the strip tightened up, and the distance z measured. The subsequent observations are collected in the following table:—

Time heated (minutes)	0	25	30	37	50	85	115	125	135	145	160
Temperature (° Pt) …	396	430	430	445	445	445	450	589	611	667	700
m/m_1 . ..	37·9	38·4	38·8	38·7	39·1	38·8	39·5	39·8	39·8	39·4	38·8

Mean $m/m_1 = 39·0$.

The above values run about 2·5 per cent. lower than those given by a fresh strip. This may mean that there is a small admixture of lighter ions which are charged atoms or molecules of gas absorbed from the air. This does not seem very likely, however, as the value is very near that given by strip No. 2 shown in fig. 1 which had been heated to about the same stage before commencing observations. It seems more reasonable to conclude that the lower values are due to a slight admixture of the ions for which m/m_1 is near the sodium value, which are apt to be present in sufficient quantity to exert some influence at this stage. It is quite clear, at any rate, that the bulk of the ions after reviving the wire by heating in air have the same value of m/m_1 as those emitted by a fresh wire.

Another platinum strip was then taken and treated somewhat similarly, except that instead of heating in air at atmospheric pressure it was taken down and heated in a bunsen flame for a few minutes. It was then found to give a large positive emission at a much lower temperature than before. The numbers given by this experiment are shown in the following table:—

Time heated *in vacuo* (minutes)	5	10	20	30	35	40	60	105	120	130	138
Temperature (° Pt)	405	405	427	473	473	473	495	506	518	541	541
m/m_1	40·2	40·1	40·2	39·0	40·7	39·6	40·6	39·6	39·9	40·2	40·0

Mean m/m_1 = 40·0.

This experiment shows that the large ionisation which is obtained when a glowed out platinum wire is heated in a bunsen flame consists of ions for which the value of m/m_1 is the same as for the ions from a freshly heated wire. This conclusion was confirmed by a repetition of the experiment but there does not seem to be any point in quoting the data which were obtained.

Two views suggest themselves as to the material origin of the ions observed in these experiments. Either the material is present in the metal all the time, to a considerable extent even after continued glowing in a vacuum, but is so securely held that it is unable to diffuse to the surface and produce ionisation. In that case the effect of heating in different gases may be imagined as resulting in a loosening up of the structure of the material by the diffusion of the gases into the interior. In this way a means would be provided for the diffusion of the ionisable material to the surface of the metal. On the other hand it is possible that the ionisable material is actually formed by the action of the gases on the heated platinum. This would involve the rather radical supposition that the atoms of the metal were being broken up by the actions occurring. I think the balance of evidence at present available is against such a view. Many years ago* I made experiments to see if a platinum wire which had lost the power of positive emission would recover it if it was allowed to remain standing in a vacuum. I only obtained small and uncertain effects. Of course, this does not prove that such actions may not occur with facility at higher temperatures. But the experimental results at present available indicate that the bulk of the positive ions given by different elements have an electric atomic weight of about 40. When one considers that this is true of the element carbon, whose atomic weight is 12, it points rather to the presence of a common impurity than to the occurrence of atomic disintegration. Moreover the following experiment shows that merely straining the metal will cause a revival of the positive emission. This, I think, supports the idea that the renewal of the emission under various circumstances is mainly a mechanical effect. I do not wish to indicate that I believe the question under discussion to be settled beyond the possibility of doubt, but I believe the balance of evidence at present available favours some such view as that just indicated.

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* 'Comptes Rendus Congrès de Radiologie,' Brussels, 1905.

The experiment referred to was made with the manganin strip, which gave a mean value of $m/m_1 = 40{\cdot}0$. After it had been heated for some time it gave an emission of 15 divisions in 30 seconds at a certain temperature. Without altering the heating current or letting down the vacuum it was found to be possible so to rotate the apparatus that the strip became inclined at 35° to the magnetic field instead of parallel to it. With the rather large heating current (0·75 ampère) which the strip was carrying, there is then a considerable pull on it due to the magnetic field. The magnetic field was rapidly reversed a number of times to get as large an effect as possible, and the emission when measured at the original temperature, which was considerably higher than that at which the straining was carried out, was found to be 308 divisions in 30 seconds. It had thus increased by a factor of more than 20. The value of m/m_1 for the ions which carried this increased emission was then measured and found to be 39·4, which agrees with the previous value within the limits of experimental error. The result of this experiment rather indicates that the revival under pressure observed by Klemensiewicz (2) may be due to the mechanical action of the pressure directly, although there are many other causes which may have played a part in an experiment of that character.

I shall now consider the remaining reasons (3) to (6) for believing in the gaseous origin of these positive ions rather more briefly. In regard to (3) I[*] at one time examined the emission of gas from a fresh platinum wire rather carefully and compared it with the simultaneous emission of positive ions. Apart from the fact that both emissions were largest at first and decayed with time there was no simple relation between them. C. J. Davisson[†] has also recently shown that there is no relation between the emission of gases by salts and the emission of positive ions from them.

As regards the greater efficiency of carbon monoxide and hydrogen (5) it is well known that both these gases have an exceptional capacity for diffusing into various metallic solids, and they would therefore be exceptionally effective, in loosening up the pores of the metal. In addition, they are both reducing agents; and reduction has been found to facilitate the emission of positive ions in the case of some salts.[‡]

So far as (6) is concerned, I myself have never been able to detect the existence of positive ions, either from fresh metals or from salts when heated in a vacuum, which have values of m/m_1 anywhere near so low as that for

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[*] 'Comptes Rendus Congrès de Radiologie,' Brussels, 1905.

[†] C. J. Davisson, 'Phil. Mag.,' 1912, vol. 23, p. 139.

[‡] O. W. Richardson, 'Phil. Mag.,' 1911, vol. 22, p. 698.

H_+ or for H_{3+}. This result has been confirmed by Davisson.[*] It seems fairly certain that with ordinary specimens of aluminium phosphate and with metals the proportion of hydrogen ions, even if there are any at all, must be much smaller than the 10 per cent. found by Garrett. This does not preclude the possibility that when a large amount of hydrogen is allowed to diffuse from the interior of an old platinum tube into air at atmospheric pressure there is a current which is carried by charged atoms of hydrogen. I[†] once concluded that this was the case; but the inference was an indirect one, and until the electric atomic weight of the carriers has been determined under these conditions one has to bear in mind the possibility that the diffusing hydrogen simply washes some heavier ionisable constituent out of the hot metal.

Turning to (4), I have made several attempts to settle, by direct measurement of m/m_1, the nature of the positive ions which are emitted when an old wire is heated in air or oxygen. The method has been to glow out a strip until the emission was very small and then to measure m/m_1 for the ions which make up the measured emission when air or oxygen at a low pressure is let into the apparatus. So far it has not been possible to get enough current to make measurements with at a low enough pressure for the method to be applicable. I do not regard this problem as insuperable, but it happens that the proper conditions have not yet been realised. In the absence of direct evidence as to the nature of these ions it would appear illegitimate to infer from their assumed nature that of other ions which are produced under different conditions.

So far the reasons which make me think the ions whose measured electric atomic weight is very close to 40 are most likely to be K_+ have hardly been considered. As a matter of fact the mean of the best values is very close to 40·0, so that either $Ar_+ = 39{\cdot}9$ or $Ca_+ = 40{\cdot}07$ would fit better than $K_+ = 39{\cdot}1$. Moreover, I am informed by manufacturers of platinum that potassium is not an impurity which one would expect to find in this metal; whereas calcium might be looked for, as the metal is heated at one stage in lime crucibles. On the other hand, any slight lack of uniformity in the electrostatic field due to the gap between the strip and the surrounding plate tends to make the measured value of m/m_1 too high. What is perhaps more convincing is the fact that the positive ions from potassium sulphate itself also gave values of m/m_1 which were too high and which agreed very well with those given initially by the hot metals. There are very good reasons for believing that the positive ions from potassium sulphate are K_+. The electric atomic weight of the ions from Li_2SO_4, Na_2SO_4, K_2SO_4, Rb_2SO_4, and Cs_2SO_4, after these salts have been heated for some time,[*] correspond respectively to Li_+, Na_+, K_+, Rb_+ and Cs_+. Moreover, on first heating Li_2SO_4, Na_2SO_4, and many other salts, the positive ions given off have a value of m/m_1 which corresponds to K_+. This shows that potassium is relatively the most efficient of the commoner alkali metals in emitting positive ions. It is a very widely distributed element, and its very marked capacity for ionisation would lead one to expect that it might give rise to the bulk of the ions emitted by the metals if the ions arise from adventitious impurities. The objection to calcium is that its efficiency does not appear to be comparable with potassium in this respect, and one would not expect Ca_+ to come off prior to Na_+, as is observed in the case of platinum. It is true that iron was found to be an exception in this respect, but the initial presence of sodium was only recorded once. This shows that at any rate there was only a small amount, which may have been caused by accidental superficial contamination. The emission of $m/m_1 = 40$ in large excess, and long before there was any considerable amount of $m/m_1 = 23$, in the case of platinum, has been amply verified in numerous experiments. In any event it is doubtful whether much attention should be paid to chemical evidence, as the amounts of matter required are extremely small in all cases. There does not, at present, seem to be any evidence other than the value of m/m_1, which would tend to support the view that these ions are charged atoms of argon, and the same may be urged against the hypothesis of heavier atoms provided with multiple charges.

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[*] C. J. Davisson, *ibid.*, p. 147.

[†] O. W. Richardson, 'Phil. Trans.,' 1906, A, vol. 207, p. 54.

In conclusion I wish to thank my former assistant, Mr. E. S. Taylerson, to whose ingenuity and manipulative skill the measure of success attained by this investigation is largely attributable.

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[*] O. W. Richardson, 'Phil. Mag.,' 1910, vol. 20, p. 981.

Absolute Measurements of a Resistance by a Method based on that of Lorenz.

By F. E. Smith, A.R.C.Sc.

(Communicated by R. T. Glazebrook, M.A., F.R.S. Received October 27,—Read December 11, 1913.

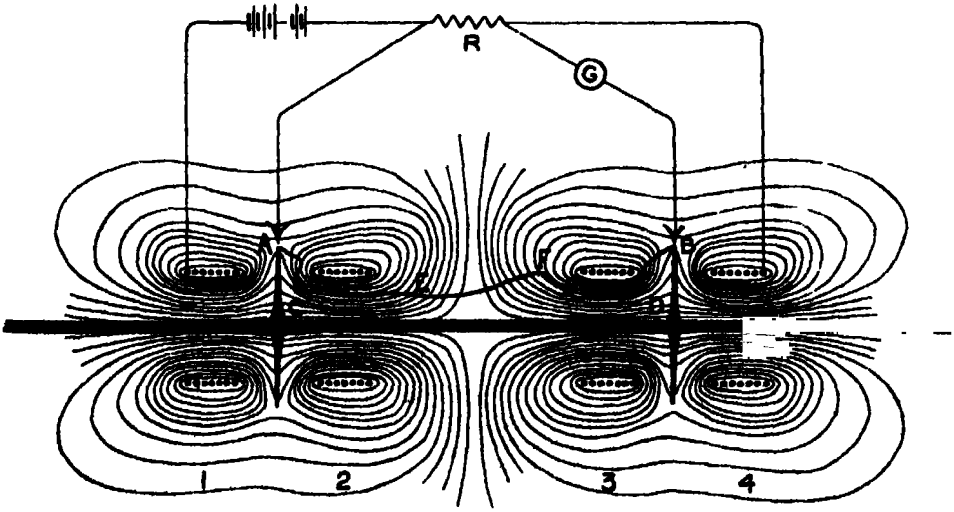
(From the National Physical Laboratory.)

(Abstract.)

The instrument described commemorates the work of the late Prof. Viriamu Jones. Its construction was rendered possible by a generous grant of money by the Drapers' Company of London, and by the kindness of Sir Andrew Noble, who provided the heavier metal portions of the instrument at very much less than the cost price.

The instrument differs from all other forms of apparatus based on the method of Lorenz, inasmuch as two discs are employed instead of one, thus practically eliminating the effect of the earth's magnetic field.

The magnetising coils are four in number. They are wound in single layers on marble cylinders, and the disposition of the coils with respect to the discs is such that the resulting magnetic fields through the discs are opposed in direction and the intensity of the field at points in the neighbourhood of the edge of a disc is of zero value, or nearly so. A diagrammatic sketch of the arrangement is shown in the figure.



Each of the two discs supports ten insulated phosphor-bronze segments placed at equal distances around its circumference, and the ten segments on one disc are connected to those on the other disc by ten conducting wires passing through the centre of the shaft. When the wires rotate with the discs a difference of potential is produced between their ends. The ten conductors are treated as five sets of two, and the five sets are at times placed in series by means of ten brushes (five to each disc), and at other times they are placed in parallel. The difference of potential produced by rotation is balanced against that on a standard resistance, R, through which the same current flows as through the coils. The resistance R can thus be found in terms of the mutual inductance of the coils and brush contact circles and the rate of rotation of the conductors. The difference of potential produced by the rotation of a conductor is dependent on the position of its ends only, and not upon its shape. Thus the difference of potential at the extremities of a conductor ACDB (see figure) is not altered if its shape is changed to AEFB.

The brushes consist of thin phosphor-bronze wires, stretched by two spiral springs, and resemble violin bows. Each brush makes contact with one or two segments over a length varying from 5 to 6 cm. and leaves a segment at a tangent, thus making the pressure greatest at the mid-point of contact. Petrol is employed as a lubricant for the brushes and is fed continuously to the surfaces of the segments.

The coils are wound with bare copper wire in double-threaded screw grooves cut on the surfaces of the cylinders. The two wires on any one cylinder form two adjacent helices, which may be connected in series or in parallel; an insulation test may be made between them. There are eight helices in all and these are connected by means of small concentric cables to a plug board and commutators, which enable the direction of the current in any coil to be changed at will.

Each cylinder is mounted on a strong metal support and its position with respect to a disc may be altered with ease by screw adjustments. The distance between the mid-planes of two coils is measured by means of microscopes.

An electric motor is used for driving. It is situated at a considerable distance from the coils and its influence as a mass of iron on the mutual inductance of the coils and brush contact circles has been experimentally shown to be not greater than one part in 10,000,000. A commutator is fixed to the axle of the motor, and this serves to charge and discharge a condenser placed in one arm of a Wheatstone bridge; by keeping the bridge permanently balanced the speed of the Lorenz apparatus is maintained constant. A directly driven chronograph enables the speed to be calculated.

Careful tests were made of the magnetic quality of all parts of the instrument, and, with the exception of the motor, I am satisfied that the magnetic permeability of no portion exceeds unity by more than two parts in 100,000.

The diameters and axial lengths of the coils were measured on three occasions and the results show that the dimensions have not changed by more than 3/1000 mm., equivalent to one part in 120,000. The diameters were measured with a current of 2 ampères circulating in the coils, and the increase in diameter produced by the heating was measured with considerable accuracy.

The diametral distance between opposite segments on a disc is about 54 cm., and when a disc rotates 1100 times per minute the diametral distance is found to increase by 0·09 mm.

The calculation of the mutual inductance of the coils and brush contact circles allows for the conicality of the coils and for the variation in pitch. Allowance is also made for the change in mean diameter of the coils during a measurement of resistance.

Electrical methods were adopted to set the coils coaxial with the shaft, and proved to be extremely sensitive. The error involved by any departure from the coaxial position may be made negligible even for measurements of high precision.

The resistances measured had nominal values of 0·001 ohm, 0·002 ohm, and 0·01 ohm. The observed values in absolute measure and the values in International ohms are given in the following table:—

No. of observations.		Resistance.			Difference, parts in 100,000. (Abs. × 10^{-9}) − (Int.).
		Standard.	Absolute measure, cm./sec.	In International ohms.	
28		0·001 ohm	100091_6	$0·00100039_3$	52_3
12		0·01 „	100090_{10}	$0·0100038_3$	51_8
5		0·002 „	Standard resistance varied		53_0
2	Coils 1 and 2 used	0·001 „	100090_4	$0·00100039_3$	51_1
2	Coils 3 and 4 used	0·001 „	100091_8	$0·00100039_3$	52_5

The International ohm is defined as the resistance offered to an unvarying electric current by a column of mercury, at the temperature of melting ice, 14·4521 grm. in mass, of a constant cross-sectional area, and of a length of 106·300 cm., while an ohm has a resistance of 10^9 cm./sec.

The agreement is most satisfactory.

The conclusion is that a resistance of 1 International ohm is equal to 1·00052 ± 0·00004 ohm (10^9 cm./sec.), the probable error of ± 0·00004 being approximately the sum of those involved in the resistance of the ohm and the International ohm. It follows that a column of mercury, at 0° C., 106·245 ± 0·004 cm. long, of constant cross-sectional area (the same as that of the International ohm), has a resistance of 1 ohm. The mass of this column will be 14·4446 ± 0·0006 grm.

I desire to express my thanks to the Drapers' Company of London and to Sir Andrew Noble for their generous help, to Lord Rayleigh for his keen interest in the work, and to Dr. Glazebrook for his very valuable help and advice throughout the investigation.

Elastic Hysteresis in Steel.

By F. E. Rowett (Whitworth Scholar), Research Student of the University of Cambridge.

(Communicated by Prof. B. Hopkinson, F.R.S. Received November 12,—Read December 11, 1913.)

The rate of dissipation of energy by internal molecular friction, when steel undergoes variations of stress within what is ordinarily regarded as the elastic limit, was the subject of a recent paper by Hopkinson and Trevor-Williams.* A bar of steel having an elastic range of about 25 tons per square inch was subjected to direct (axial) push and pull, the limits of tension and compression being equal, and the frequency of the cycles about 120 per second. The dissipation of energy by elastic hysteresis was determined by the fall of temperature between the middle point of the bar and the ends. It could be measured accurately in this way when the range of stress was near the elastic limit (25 tons per square inch) and could be detected when the range was 10 tons per square inch.

One object of the research just referred to was to ascertain whether the dissipation of energy per cycle of stress increased with the speed of reversal, in other words whether the internal friction to which this dissipation is

* 'Roy. Soc. Proc.,' A, vol. 87, p. 502.

due is of the nature of solid friction, or is more analogous to the viscosity of fluids. For this purpose the bar was alternately compressed and extended, statically, in a testing machine, between the same limits of stress as in the high-speed tests, and the stress-strain curve was obtained by means of a specially designed extensometer.

The curve is of course a very narrow loop, the area of which corresponds to the dissipation of energy in the slow-speed cycle. It was not found possible to do more than determine the width of this loop at the origin, corresponding to the difference in length of the unstressed piece according as the last application of stress had been compression or tension. The area of the loop is equal to the product of this difference into the range of strain, multiplied by a constant which depends on the shape of the loop. In the paper under consideration it was assumed that the loop was of lenticular form, being bounded by two arcs of circles of large radius, and on that assumption the hysteresis in the static test was at all stress ranges about 1·25 times that found in the high-speed cycle between the same limits of stress. As pointed out in the paper, the uncertainty as to the shape of the loop precluded any very definite inference as to the effect of speed of reversal on hysteresis except that the difference, if any, was probably in the direction of reduced hysteresis at high speeds, and that it was not more than 30 per cent. as between 120 cycles per second and quite slow reversals.

The present research is a further study of this problem. In order to secure higher accuracy in the measurement of the static hysteresis, thin-walled tubes have been used in torsion. By the use of spirit levels in the manner described in greater detail below, it has been found possible to detect shearing strains of the order of 10^{-6}, corresponding to a stress of 12 lb. per square inch, and to determine within about 5 per cent. the energy dissipated by elastic hysteresis in a cycle of stress well within the elastic limit. The corresponding high-speed cycles were observed by the method of torsional oscillations, first employed by Lord Kelvin. One end of the tube was fixed, and a fly-wheel was mounted on the other end, of such inertia as to give a frequency of torsional vibration of about 70 per second, and the amplitude of vibration was recorded photographically. From the rate of decay, after correcting for air-friction, the hysteresis loss is calculated.

Briefly, the result of these experiments is to show that the hysteresis is, probably within 5 per cent., the same at high speeds as at low speeds. Furthermore, the shape of the hysteresis loop, which was left uncertain by Hopkinson and Trevor-Williams' work, has been determined. If the constant giving the area of the loop from its principal dimensions, which has been determined by the present author for torsional cycles, be substituted for the conjectural constant used by them, the result is to bring the hysteresis of their static cycles into almost exact agreement with that which they found at high speeds.

It also appears that in a hard drawn tube as supplied by the makers the hysteresis is for all stress-ranges only about one-eighth of the hysteresis in the same tube after it has been softened by annealing. In the annealed tube the loss per cubic centimetre per cycle, with a stress-range in shear of 1160×10^6 dynes per square centimetre (7·5 tons per square inch), is about 11,000 ergs, and it varies approximately as the cube of the stress-range.

Hopkinson and Trevor-Williams found at the corresponding range of stress a loss of about 4000 ergs in a steel bar which had not been annealed, and at higher stresses the loss in their experiments varied as the fourth power of the stress-range.

High-speed Cycles.

The material was in the form of tubes having a mean external diameter of 0·625 inch, and a mean thickness, determined by weighing, of 0·0475 inch.

The steel had the following composition:—Carbon, 0·17 per cent.; manganese, 0·24 per cent.; sulphur, 0·02 per cent.; phosphorus trace, the remainder being iron.

The tubes, as they came from the makers, were hard, as the result of the drawing. The elastic limit in torsion in this state was 13·8 tons per square inch shear stress in either direction, giving an elastic range of 27·6 tons in shear or 55 tons in tension and compression. By annealing at 800° C. for fifteen minutes and cooling in the furnace the effect of the drawing was removed. The tubes were then quite soft and ductile and had a well-marked yield point in torsion of 5·58 tons per square inch shearing stress, the elasticity as determined by ordinary tests being nearly perfect up to that stress. The elastic range in this condition is, therefore, roughly 11·2 tons per square inch in shear or 22·4 tons per square inch in tension and compression.

The specimen tube AB was firmly fixed at B, fig. 1 (thorough and smooth soldering was found to be efficient), into a steel block, which in turn was securely bolted down to a cast-iron frame of very massive proportions. The upper end of the tube was fixed into a small flywheel, the whole being arranged with the tube vertical, as shown in fig. 1. Four very small stops were fitted into the flywheel, two being utilised for applying a pure torque by means of stirrups E and F. Cords passed from the stirrups over pulleys fitted with ball-bearings, and were attached to scale pans G and H.

The two columns M and N were fitted with adjustable centres, about which the ring PQ could be rotated. This ring carried two stiff, fine-threaded screws which engaged with the remaining two stops on the flywheel. The latter were fitted so that the upper edge of one and the lower edge of the other coincided with each other and with the centre of the flywheel. The heights of the adjustable centres were set so that upon rotating the ring the screws left the stops, the one at the upper edge and the other at the lower edge, at the same instant.

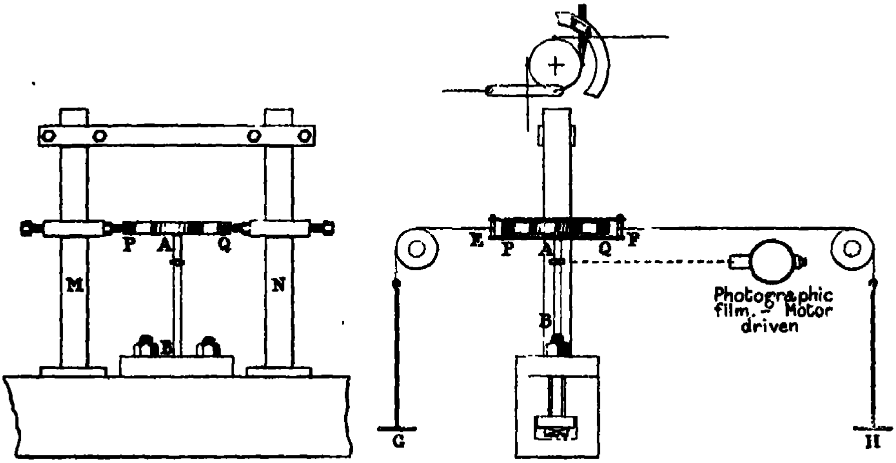


FIG. 1.

A mirror was attached to the tube at a definite distance from the fixed end, and records were taken of its motion upon motor-driven photographic films. In making an experiment, a definite torque was applied to the tube by means of weights and stirrups, and the screws adjusted so as just to take the stress on turning the ring into position.

This could be conveniently done by observing the spot of light, any movement of the spot on turning the ring indicating a faulty adjustment. The weights and stirrups were now removed without disturbing the distribution of stress in the tube.

A record was finally obtained by rotating the ring clear of the stops and thus releasing the flywheel, which was thereby set in torsional vibration.

A calibration was taken upon the same film by applying the same torque and obtaining the deflection in the form of a continuous line on the film, the ring meanwhile remaining free, so that the calibration was independent of the setting or the adjustments.

It was found that 1 cm. deflection corresponded to a stress of 229×10^6 dynes per square centimetre, *i.e.* about 1·48 tons per square inch.

The effect of air friction was investigated by fixing a small steel post above the flywheel to which was attached a disc of thin sheet tin. Films were obtained with the tin disc attached and also without the tin disc for the same specimen, and the increased damping obtained by difference. The air-friction was found to be small by comparison when the steel tube used had been annealed. The tubes, however, as supplied were in a hardened state due to the process of manufacture, and in this condition the dissipation of energy in the specimen was found to be considerably less than in the annealed state. Advantage was taken of this fact to determine the energy lost by air friction.

The friction loss is due almost entirely to the vibration of the flywheel, the motion of the tube being very small indeed. The flywheel was a plain smoothly turned disc, and the friction loss per cycle was assumed to be the same as that of a disc of the same diameter of tin plate with a rim attached, the width of the rim being equal to half the thickness of the flywheel. The disc was attached at a distance sufficiently away from the flywheel to avoid any interaction, and the two had exactly the same motion.

The weight of the disc was so small in comparison to the flywheel that the frequency of vibrations was altered by only a very small amount (about 0·25 per cent.). The damping curves obtained are shown in fig. 2. The amount of energy stored in the flywheel and tube per cubic centimetre of steel is equal to the (stress-range) ^{2}/8 C ergs, where C is the modulus of rigidity, the stress-range and C being both expressed in dynes per square centimetre.

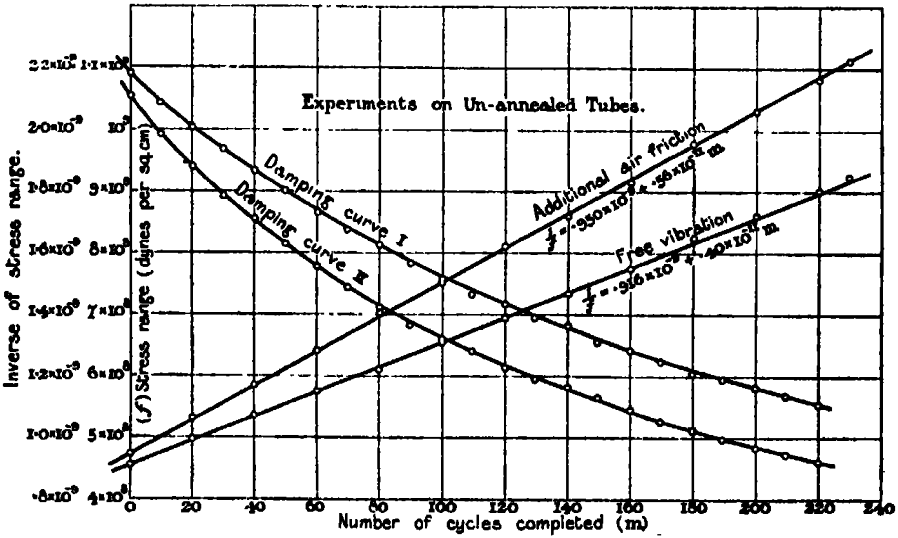


Fig. 2.

Let x = amplitude, which is proportional to the range of stress, and suppose the energy lost per cycle $\propto x^m$. Then the loss of energy per second is given by

$$nx^m \times \mathrm{A} = \mathrm{B}x\dot{x},$$

where n = number of cycles per second and A and B are constants; the integral of which is

$$t = \frac{\mathrm{B}}{n\mathrm{A}} \cdot \frac{1}{(2-m)} \{x^{2-m} - x_0^{2-m}\},$$

where x_0 is the amplitude when $t = 0$.

If $m = 3$, corresponding to the law friction $\propto$ velocity^2, the law of variation of amplitude is given by

$$t = \lambda\left[\frac{1}{x} - \frac{1}{x_0}\right], \text{ where } \lambda = \text{constant},$$

that is the inverse of the stress-range plotted against the number of cycles performed should give a straight line. The latter has been done for the curves above and the results are shown plotted in fig. 2. Straight lines were obtained both for free vibrations and also when the additional air disc was attached.

The equations of the lines were found to be

I. Free vibration............... $1/f = 0{\cdot}916 \times 10^{-9} + 0{\cdot}40 \times 10^{-11} m$,

II. Additional air friction ... $1/f = 0{\cdot}950 \times 10^{-9} + 0{\cdot}56 \times 10^{-11} m$,

where f = stress range in dynes per square centimetre, and
m = the number of cycles performed.

The energy present per cubic centimetre of metal $= \frac{1}{8}f^2/\mathrm{C}$ ergs, where C = modulus of rigidity.

From Equation I $\quad -\dfrac{1}{f} \cdot \dfrac{df}{dm} = 0{\cdot}40 \times 10^{-11}$,

" " II $\quad -\dfrac{1}{f} \cdot \dfrac{df}{dm} = 0{\cdot}56 \times 10^{-11}$.

The energy lost per cycle per cubic centimetre $= -\dfrac{f}{4\mathrm{C}} \cdot \dfrac{df}{dm}$ ergs.

$\mathrm{C} = 82{\cdot}8 \times 10^{10}$ dynes per square centimetre (12×10^6 lb. per square inch).

Therefore from I the energy lost per cubic centimetre per cycle is

$$1{\cdot}208 \times 10^{-24} \times f^3 \text{ ergs},$$

and from II $\quad 1{\cdot}691 \times 10^{-24} \times f^3$ "

The energy in ergs per cubic centimetre per cycle lost by air friction is therefore

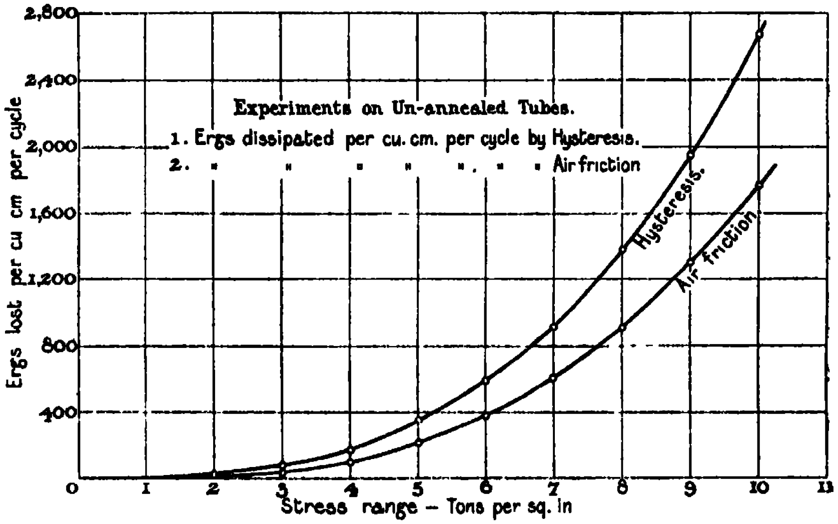
$$0{\cdot}483 \times 10^{-24} \times f^3 \text{ ergs},$$

and by hysteresis $\quad 0{\cdot}725 \times 10^{-24} \times f^3$ "

f being in dynes per square centimetre. If f be expressed in tons per square inch,

Hysteresis loss $= 2{\cdot}677 \times f^3$ ergs per cubic centimetre per cycle.
Air frictional loss $= 1{\cdot}783 \times f^3$ „ „ „

Fig. 3 shows the results plotted. The frequency of the vibrations in the above experiments was 67 cycles per second.



67 cycles per second.

Fig. 3.

Experiments with Annealed Tubes.

Some of the tubes employed were annealed by gradually heating them throughout their length to a temperature of 800° C in an electric furnace, maintaining this temperature for about 15 minutes, and then allowing them to cool in the furnace. The cooling took about 4 hours.

For the same stress-range the damping was found to have considerably increased and Table I gives the dissipation in ergs per cycle at the various stress-ranges, while fig. 4 shows results plotted. The length of the tube employed was the same as in the previous experiments and the frequency was found to be the same. Column 7 gives the calculated dissipation due to air friction and the hysteresis loss is obtained by difference.

It will be seen from fig. 4 that at a stress-range of 1160×10^6 dynes per square cm. (7·5 tons per square inch) the hysteresis loss per cubic centimetre per cycle is 11,000 ergs, whereas the air friction loss is 740 ergs or about 6·7 per cent.

Table I.—Experiments on Annealed Tubes. Annealed at 800° C. and Cooled in Furnace. Vibrations 67 per sec.

No. of cycles.	Amplitude.	Stress-range.	Energy.	Mean stress.	Dissipation.	Correction, air friction.	Hysteresis.
	cm.	tons per sq. in.	ergs.		per cycle.		ergs per cycle.
0	5·17	7·82	$2·201 \times 10^5$	7·60	11,950	770	11,180
2	4·88	7·38	$1·962 \times 10^5$	7·19	10,050	660	9,390
4	4·62	6·99	$1·761 \times 10^5$	6·83	8,050	560	7,490
6	4·41	6·67	$1·600 \times 10^5$	6·51	7,200	480	6,720
8	4·21	6·36	$1·456 \times 10^5$	6·22	6,450	417	6,033
10	4·02	6·08	$1·327 \times 10^5$	5·93	5,950	360	5,590
12	3·83	5·70	$1·208 \times 10^5$	5·66	5,300	312	4,988
14	3·66	5·54	$1·102 \times 10^5$	5·42	4,650	280	4,370
16	3·50	5·30	$1·009 \times 10^5$	5·17	4,550	236	4,314
18	3·34	5·05	$0·918 \times 10^5$	4·94	3,950	200	3,750
20	3·19	4·83	$0·839 \times 10^5$	4·39	2,800	132	2,068
30	2·62	3·94	$0·559 \times 10^5$	3·57	1,911	76	1,835
40	2·11	3·20	$0·368 \times 10^5$	2·91	1,221	44	1,177
50	1·78	2·62	$0·246 \times 10^5$				

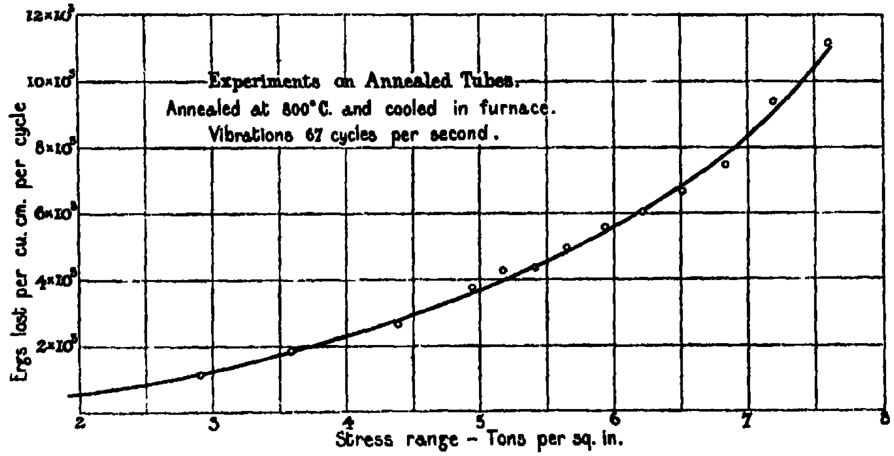


FIG. 4.

Order of Accuracy in Dynamical Experiment.

The amplitudes of the vibrations upon the photographic films could be measured to 1/5 mm., so that, at the maximum range of about 5 cm., the possible error did not exceed 1/250 in the amplitude or 1/125 in the energy. This amounts to 1600 ergs per cubic centimetre.

The dissipation is calculated by obtaining the energy present every two complete cycles, taking the difference and dividing by two.

The difference at the higher ranges amounts to about 20,000 ergs, so that the possible error in the measurement of energy dissipated in any one cycle does not exceed 8 per cent.

In the fair curve drawn through the plotted points for this quantity in terms of the number of cycles completed, the accidental errors of observation disappear in large measure and the error at the higher stresses probably does not exceed 4 per cent.

Static Experiments.

Static tests were performed upon the tubes used in the dynamical experiments, with the object of finding the actual shapes and areas of the hysteresis loops for various stress-ranges when these were performed slowly by hand.

The method employed was to submit the tube to cyclic stress-ranges performed in the direction of the arrows, fig. 5. After a number of cycles the process was stopped at a point E and the strain measured. The cycle was then continued until the point F was reached having exactly the same stress but being in the opposite portion of the loop.

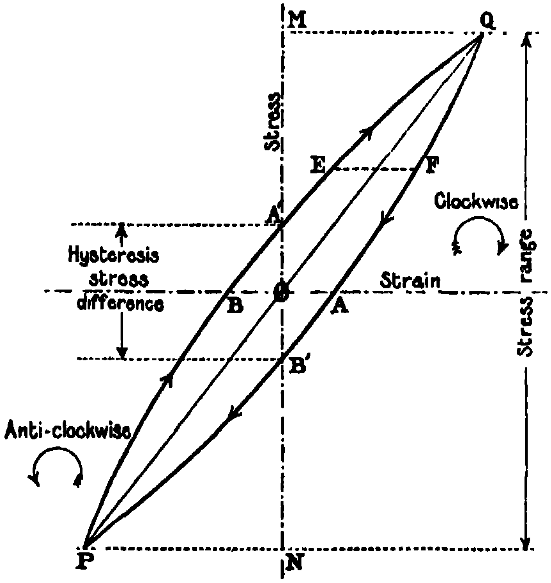


Fig. 5.

The strain was again measured and the difference between the then value and the previous value for the same stress gave the length EF.

By varying the position of the points E and F and meanwhile keeping the stress-range constant the exact shape of the loop for this range was obtained.

The difficulty in such experiments of eliminating completely the effects of friction and hysteresis in the apparatus which is used for measuring stress was overcome in this case by fixing the tube under experiment at one end to a much longer and stronger hard drawn tube, through which the torque was applied, and by the twist of which it was measured. The dimensions of the tube were such that the stress in it was about 1/7th of that in the small tube.

Since the hysteresis stress difference (measured by A′B′, fig. 5) varies approximately as the square of the stress-range, the value of the stress difference in the large tube was about 2 per cent. of its value in the small tube. The hysteresis in the large tube was removed by applying a small torque until the actual twist in the large tube was zero. This small torque, however, removed some of the twist due to hysteresis in the small tube, and the hysteresis observed in the small tube was thus smaller than the actual value by 14 per cent. when both tubes were in the hard drawn condition. When the small tube was annealed and the other hard drawn the error was about 1·8 per cent.

Static Apparatus.

The stiff tube was rigidly fixed at one end and the torque was transmitted to it through the experimental tube. The lengths of the tubes were such that the angular twist in each was approximately the same. Fig. 6 gives a general view and details of the apparatus. The compound tube GH was rigidly fixed at G, while the end H was keyed to lever L working between adjustable stops E and F. Sensitive micrometer levels, fig. 6 (*a*), were fixed to the tubes at the positions A, B, C, and D, and at M_1 and M_2 small plane mirrors, fig. 6 (*b*), were arranged so that reflections from scales S_1 and S_2 were observed in telescopes T_1 and T_2 respectively.

The weights W exactly balance the weight of lever L. The mirrors M_1 and M_2, in conjunction with the telescopes and scales, supply the means of measuring the extreme ranges of strain, and thus of stress.

In making an experiment the desired torque is applied to lever L, fig. 6, and by means of the micrometer screws all four levels are adjusted so that the bubbles read zero. The desired cycle of stress is then applied by movement of lever, which is returned approximately to its original position, and there adjusted by means of screw P until the two levels A and B again read exactly zero.

If the hysteresis in the large tube is neglected the torque is now precisely the same as before. The levels C and D will now no longer read zero, and the difference between them represents the hysteresis corresponding to the cycle of stress which has been performed (*i.e.* length EF in fig. 5).

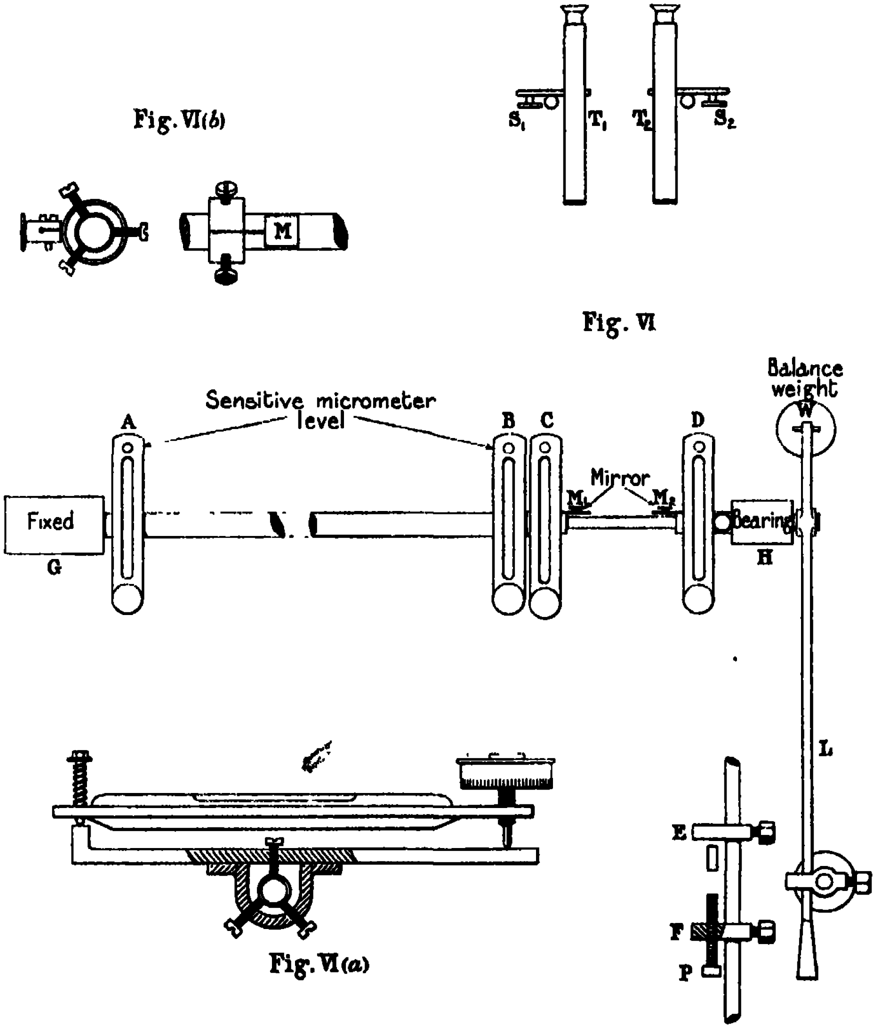


FIG. 6.

Shape of the Loop.

To obtain a comparison between the hysteresis at high frequency and that obtained by static experiments, it is necessary to know the area of the loop, that is to obtain the relation between the maximum and mean widths.

This has been done in the following manner :—A definite stress-range was first decided on, and the stops E and F adjusted as required, the range being calculated as before from the mirror readings at the extreme positions of lever L.

After a few hundred cycles had been performed at this range, in order to get the material into a cyclic state, the process was stopped at a definite point in the cycle and the stress maintained by means of screw P. All the levels were now adjusted to read zero and the readings of the telescopes noted. From the latter and a knowledge of the readings for zero stress, the position in the cycle was ascertained. The cycle was now continued to one extreme position and the lever brought back and screw P adjusted until levels A and B were again zero. This occurs (neglecting hysteresis in the large tube) when the stress in the large tube, and therefore in the small tube, is exactly the same as before. The levels C and D were now found to have readings other than zero, showing that the strain in the tube is slightly different from what it was before.

Table II gives the results for a cycle covering a range of 7·86 tons per square inch (±3·93 tons). The last column but one gives the difference of twist observed at various points in the cycle, according as the stress is increasing or decreasing. The last column gives the corresponding stress difference, and is obtained by multiplying the strain in the preceding column by the modulus C. These results are shown graphically, the figure representing the hysteresis loop being magnified 40 times in the direction of the stress axis. It should be noted that in setting out the figure it is assumed that the observed stress difference, such as RS, fig. 7, is bisected by the line PQ which corresponds to perfect elasticity. This assumption is, of course, not necessarily true, and to this extent the real shape of the loop is uncertain, but it does not affect the area of the loop, which it is the main object of these experiments to determine. The mean width of the loop is 0·506 of the maximum width, and the area in ergs of the cycle is to be obtained by multiplying the maximum width on the stress axis by the range of strain and by the constant 0·506. Hopkinson and Trevor-Williams assumed this constant to be 2/3, and the dissipation for high-speed cycles then appeared to be 0·8 times that observed in the statical experiments. The use of the factor 0·506 in reducing the results of the latter brings the two into close agreement. Another experiment at a range of 6 tons per square inch gave the same ratio of maximum to mean width within 1 per cent. At lower stress-ranges the accuracy is not sufficient to determine the shape of the loop but it may be assumed that it is substantially independent of the stress-range, and that the area may be calculated from the width of the loop at zero stress by the use of this same constant. This width was determined for a number of stress-ranges. The procedure was exactly the same as described above, the only points determined in each case, however, being those corresponding to zero or approximately zero stress.

The results are plotted in fig. 8. The corresponding loop areas calculated from the maximum widths by the use of the constant 0·506 gave when plotted the curve shown in fig. 9. On the same figure are shown the values of the energy dissipated per cycle at 67 cycles per second, as determined with the dynamic machine. It will be seen that the two agree very closely.

Table II.—Experiments on Annealed Tubes. Shape of Hysteresis Loop. Stress-range 7·86 tons per sq. in.

Mirror readings.		Equivalent stress.	Level readings.		Equivalent micrometer readings.		Difference.	Strain lag twist in radians.	Width of loop
			C.	D.					
		Tons per sq. in.							Tons per sq. in.
11·32	9·80	3·56	0	0·4	0	0·31	0·31	$0{\cdot}033 \times 10^{-3}$	0·0055
12·32	11·13	3·05	0·05	1·6	0·04	1·25	1·21	$0{\cdot}129 \times 10^{-3}$	0·0216
13·32	12·47	2·595	0·1	2·75	0·07	2·14	2·07	$0{\cdot}221 \times 10^{-3}$	0·0370
14·32	13·80	2·20	0·1	3·80	0·07	2·97	2·90	$0{\cdot}309 \times 10^{-3}$	0·0517
15·32	15·11	1·772	0·2	5·0	0·14	3·90	3·76	$0{\cdot}401 \times 10^{-3}$	0·0672
16·32	16·46	1·303	0·3	6·4	0·22	5·00	4·78	$0{\cdot}510 \times 10^{-3}$	0·0853
17·32	17·77	0·878	0·3	7·3	0·22	5·61	5·47	$0{\cdot}584 \times 10^{-3}$	0·0977
18·32	19·11	0·401	0·4	8·1	0·29	6·32	6·03	$0{\cdot}643 \times 10^{-3}$	0·1075
19·33	20·42	Nil	0·4	8·8	0·29	6·86	6·57	$0{\cdot}701 \times 10^{-3}$	0·1172
20·34	21·72	0·398	0·4	8·1	0·29	6·32	6·03	$0{\cdot}643 \times 10^{-3}$	0·1075
21·34	23·06	0·874	0·3	7·4	0·22	5·77	5·55	$0{\cdot}594 \times 10^{-3}$	0·0995
22·34	24·37	1·293	0·3	6·4	0·22	5·00	4·78	$0{\cdot}510 \times 10^{-3}$	0·0853
23·34	25·72	1·77	0·2	5·1	0·14	3·98	3·84	$0{\cdot}409 \times 10^{-3}$	0·0683
24·34	27·08	2·19	0·1	3·8	0·07	2·97	2·90	$0{\cdot}309 \times 10^{-3}$	0·0517
25·34	28·36	2·606	0·1	2·8	0·07	2·18	2·11	$0{\cdot}225 \times 10^{-3}$	0·0370
26·34	29·70	3·10	0	1·5	0	1·17	1·17	$0{\cdot}125 \times 10^{-3}$	0·0209
27·34	31·03	3·58	0	0·4	0	0·31	0·31	$0{\cdot}033 \times 10^{-3}$	0·0055

Table III.—Experiments on Annealed Tubes. Annealed at 800° C. and Cooled in Furnace.

Setting mirror readings.			Equivalent stress-range.	No. of cycles.	Level readings.		Equivalent micrometer readings.		Difference.	Angle of twist, radians.	Hysteresis stress difference.	Area of cycle.
					C.	D.						
			Tons per sq. in.								Tons per sq. in.	ergs.
Top ... Bottom	29·22 10·32	31·98 6·79	8·53	100	0·4	11·0	0·29	8·57	8·28	$0{\cdot}844 \times 10^{-3}$	0·148	18,350
Top . . Bottom	28·40 11·32	30·88 8·11	7·67	100	0·4	8·2	0·29	6·39	6·10	$0{\cdot}651 \times 10^{-3}$	0·109	12,180
Top . Bottom	27·80 11·80	30·10 8·78	7·22	100	0·3	7·2	0·22	5·61	5·39	$0{\cdot}575 \times 10^{-3}$	0·0964	10,120
Top . Bottom	27·20 12·33	29·32 9·50	6·73	100	0·3	6·15	0·22	4·80	4·58	$0{\cdot}489 \times 10^{-3}$	0·0819	8,020
Top .. Bottom	26·79 12·79	28·75 9·97	6·51	100	0·2	5·5	0·14	4·29	4·15	$0{\cdot}442 \times 10^{-3}$	0·0741	7,020
Top . Bottom	26·19 13·37	27·95 10·69	5·78	100	0·15	4·6	0·11	3·59	3·48	$0{\cdot}371 \times 10^{-3}$	0·0621	5,220
Top ... Bottom	24·81 14·68	26·13 12·63	4·61	100	0·1	3·2	0·07	2·50	2·43	$0{\cdot}259 \times 10^{-3}$	0·0434	2,900
Top ... Bottom	24·15 15·37	25·27 13·57	3·97	100	0·1	2·6	0·07	2·03	1·96	$0{\cdot}209 \times 10^{-3}$	0·0350	2,020

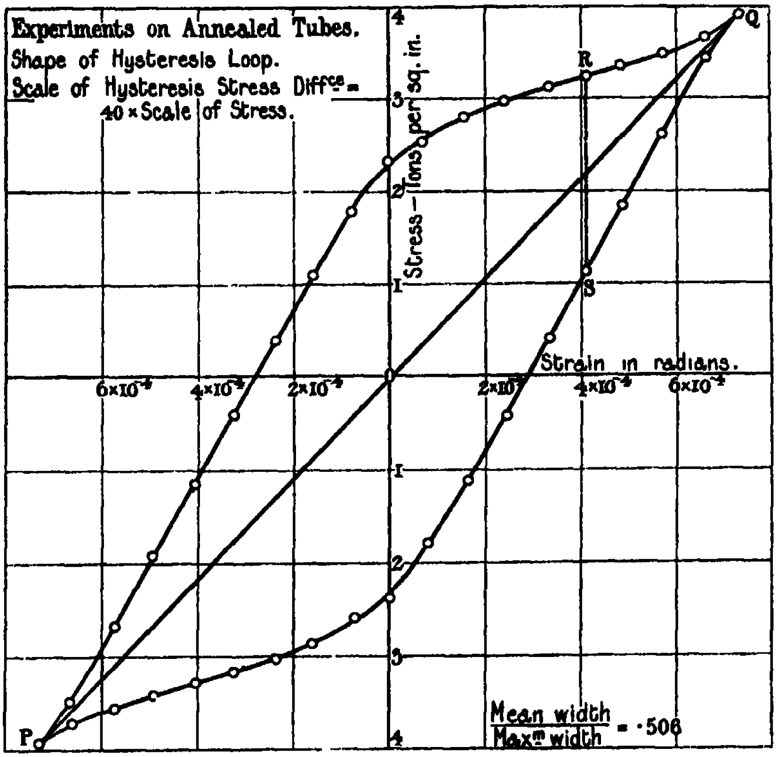


FIG. 7.

Unannealed Tubes.

An unannealed tube was introduced into the static apparatus and readings taken for the width at the mid-point of hysteresis loop.

It was found as might be expected from the high-speed experiments that the hysteresis was very small except at high ranges of stress. The following value is given as illustration :—

Stress-range, 8·52 tons per square inch ($13·17 \times 10^8$ dynes per square centimetre).

Width of loop at centre, 0·015 ton per square inch.

Area of loop, 1820 ergs.

At the same stress-range the dissipation found in the high-speed machine was 1650 ergs (see fig. 3). The difference between this result and that obtained statically is within the errors of experiment.

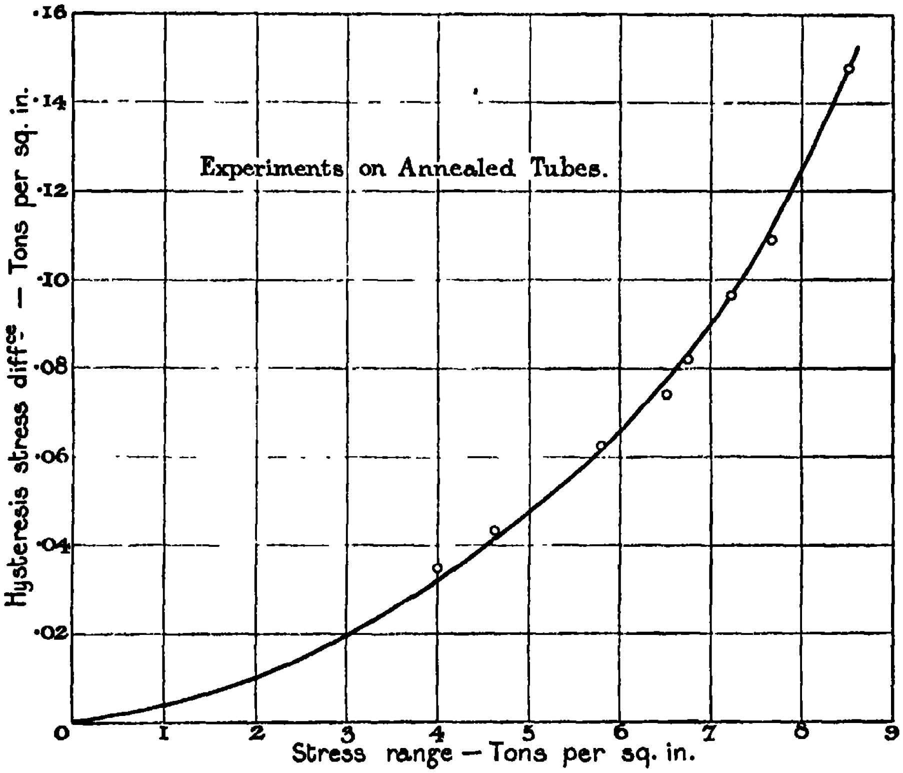


Fig. 8.

Order of Accuracy in the Static Experiments.

The levels used were placed 10 inches apart upon the experimental tube, and when in position the levels were calibrated against rotation of micrometer heads. The divisions on the levels were about ⅛ inch long and readings of these could be easily estimated to ⅕th of a division.

One division of the levels required, taking the mean value of levels C and D, 0·75 of a thousandth on the micrometer head.

Thus ⅕th division $= \dfrac{0{\cdot}15}{1000}$ in.

The micrometer head worked upon a radius of 9⅜ inches, so that the angle of twist could be accurately estimated to within

$$\frac{0{\cdot}15}{1000} \times \frac{8}{75} = \frac{8}{500{,}000} \text{ radians.}$$

The angle of shear $\phi = r\theta/l$ could be thus estimated to

$$\frac{8}{500{,}000} \times \frac{5}{160} = \frac{1}{2 \times 10^6} \text{ radians.}$$

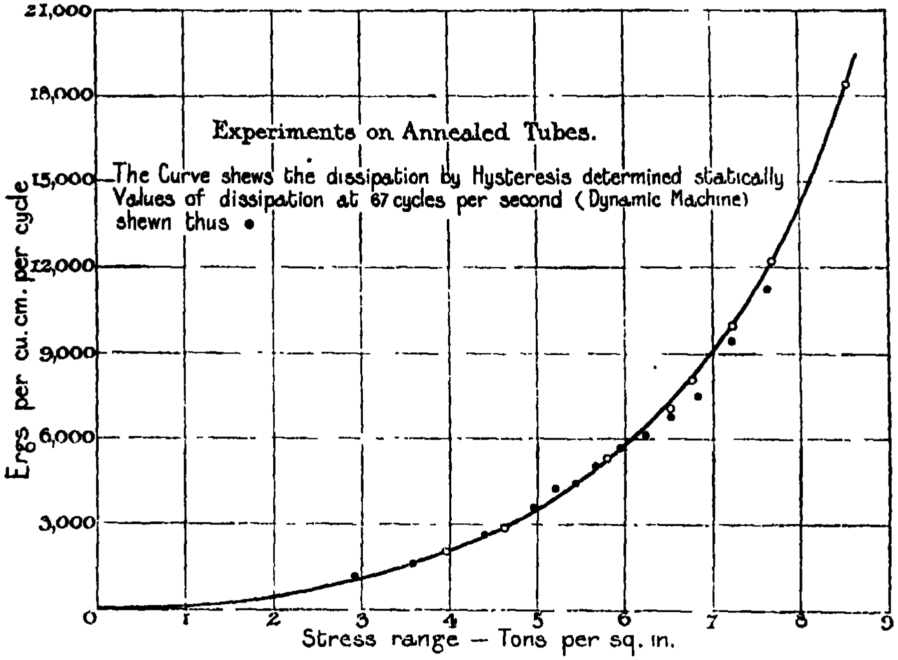


FIG. 9.

Assuming $C = 12 \times 10^6$ lbs. per square inch, the hysteresis stress difference could be calculated to within

$$12 \times 10^6 \times \frac{1}{2 \times 10^6} = 6 \text{ lb. per square inch.}$$

For a stress range of 7·67 tons per square inch the hysteresis stress difference is 0·109 ton per square inch (244 lb. per square inch) so that by means of the apparatus described above the width of the loop at the mid-point for this range can be estimated correct to within 2½ per cent. of itself.

The above work was carried out at the Engineering Laboratory, Cambridge, and I wish to express my thanks to Prof. B. Hopkinson for his kind help and inspiring interest.

Studies in Brownian Movement. I.—*On the Brownian Movement of the Spores of Bacteria.*

By John H. Shaxby, B.Sc., and E. Emrys-Roberts, M.D.

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(From the Department of Pathology and Bacteriology, University College, Cardiff.)

I. Brownian movement, the persistent and irregular motion of small particles suspended in a fluid, has been shown by the work of Wiener,[*] Jevons,[†] Gouy,[‡] and others to be independent of such conditions as vibration, intensity of illumination and convection currents; it occurs equally at the surface of the earth and in deep cellars or tunnels. Its activity, in fact, seems to depend only on the size of the particles, and upon the temperature and viscosity of the fluid in which they are suspended. These facts led Wiener, and subsequently several others, to attribute the movements to the molecular motion of the fluid, of which the particles thus act as indicators.

In 1905 Einstein[§] embodied this theory in a definite form: he showed that the total displacement of a particle in any given horizontal direction in a given time is proportional to the square root of that time, and is given by the equations

$$D = X^2/2t = RT/6\pi r\eta N,$$

in which D = coefficient of diffusion, X^2 = mean square of displacement in the direction of an arbitrary horizontal axis in time t, T = absolute temperature, r = radius of a particle, η = viscosity of suspending fluid, R = the gas constant $83 \cdot 2 \times 10^6$, and N = Avogadro's constant, the number of molecules in a gramme-molecule of a gas. Thus measurements either of D or of X and t, together with a knowledge of T, r, and η, allow N to be calculated, and its value compared with that obtained by other methods.

The correctness of this theory has been strikingly confirmed by the series of experiments carried out by Perrin and his fellow workers.[||] They have used both measurements of the coefficient of diffusion and of the displacement of particles in a given time in their verifications, and have also examined rotatory Brownian movement, for which Einstein[*] also supplied the theory. Perrin's first experiments were made upon the statistical equilibrium of suspensions. Small particles of equal size suspended in a fluid of density less than their own tend to settle to the bottom of the fluid; this tendency is opposed by their Brownian movement, which, if it were not for gravity, would distribute them evenly throughout the fluid. The net effect is thus a distribution exactly similar to that of the air molecules in an isothermal atmosphere; the number of particles in a given horizontal layer is statistically constant as soon as a kinetic equilibrium has been established, and the ratio of the numbers in any two strata at a vertical distance h apart is given by the equation, for suspensions,

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[*] 'Pogg. Ann.,' 1863, vol. 118, p. 79.

[†] 'Proc. Manch. Soc.,' 1869, vol. 9, p. 78.

[‡] 'Journ. de Phys.,' 1888, vol. 7, p. 561.

[§] 'Ann. der Physik,' 1905, vol. 17, p. 549.

[||] 'Comptes Rendus,' 1908, vol. 146, p. 967; 1908, vol. 147, p. 475; 1909, vol. 149, pp. 477 and 549; 1911, vol. 152, pp. 1380 and 1569; 'Ann. de Chim. et de Phys.,' 1909, Ser. 8, vol. 18, p. 5.

$$\log \frac{n_0}{n} = \frac{\mathrm{NV}}{\mathrm{RT}} (\Delta - \delta) gh,$$

where n_0 is the mean number per unit volume measured at the lower level, n that at the upper level, Δ and δ the densities of the material of the particles and of the fluid respectively, and V the volume of each particle. The numbers n_0 and n of this equation and X in that of Einstein's theory were determined by microscopic observations of suspensions enclosed in a glass cell. The suspensions were bounded both at bottom and top by the glass of the microscope slide and cover-slip respectively; the observations were thus made on what we call below "enclosed drops."

The mean values of $\mathrm{N}/10^{22}$ determined were:—

Equilibrium of suspensions	68·2
Brownian movement of translation ...	68·8
Brownian movement of rotation	65
Diffusion of suspensions	69

The conditions were varied in the series of experiments to the following extent:—

Mass and volume of particles, in the ratio of 1 to 70,000 and 1 to 90,000 respectively.

Viscosity of liquid, 1 to 330.

Difference, $\Delta - \delta$, between densities of particles and liquid, 1 to 30.

Temperature, from $-9°$ C. to $58°$ C.

Nature of suspending liquid: water; sugar and urea solutions; glycerine, pure and diluted with water.

Nature of suspended particles: gamboge and mastic.[†]

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[*] 'Ann. der Physik,' 1906, vol. 19, p. 371.

[†] J. Perrin, 'Les Atomes,' Lib. Felix Alcan, 1913, 3rd Edit., p. 188.

These variations would appear to be amply sufficient for a satisfactory test with the exception of the last. The mere agreement of the results obtained with two such similar substances as mastic and gamboge, both resins, is not in itself of much value. The close accordance of the value of N obtained in these various experiments with the values derived from entirely different methods is however strongly in favour of Einstein's theory, as a complete, and not merely an approximate, quantitative description of Brownian movement. The opinion of other observers, that the movements are independent of the nature of the suspended particles, though not supported by exact measurements, must yet be accorded some value. Nevertheless it seems desirable to examine the behaviour of particles quite different from resins, and particularly to investigate any apparent anomalies in Brownian movement.

II. In a previous paper* by one of us and Dr. S. B. Walsh, it was recorded that the spores of certain bacteria in suspension in various liquids did not show Brownian movement. The spores examined, those of *Bacillus anthracis*, *B. subtilis* and others, are approximately ellipsoidal, of dimensions about $1{\cdot}2\mu \times 1\mu \times 1\mu$. The observations were made upon hanging-drop preparations.

The spores forming the suspensions at first exhibited Brownian movement, but after a short time a very large proportion of them became entirely stationary. Small particles of other substances, such as carbon, and non-motile cocci, such as *Staphylococcus aureus*, of about the same size, in exactly similar preparations, continued in Brownian movement indefinitely.

The immobility of the spores was shown to be independent of temperature and occurred in water, in saline solutions, in formol solutions, and in dilutions of glycerine of marked differences of density and viscosity. The immobility was also found to take place whether the spores were living or had been previously killed by heat.

The only way in which it was found possible to inhibit the immobility of spores in hanging-drop preparations was by treating them with antiformin (solution of sodium hydrate and sodium hypochlorite), a strongly alkaline liquid with great powers of attacking organic matter. After this treatment spores showed persistent Brownian movement comparable with that of ordinary particles. Acids were without effect; the characteristic immobility appeared as usual in hanging-drop preparations of spores which had been treated with 50-per-cent. hydrochloric acid for 48 hours.

III. The further observations to be recorded show that in a hanging-drop preparation the immobile spores form a layer, one spore thick, at the air-water interface, movement in the plane of the interface as well as in the vertical direction being completely arrested. In the course of time these immobile spores congregate, still at the interface and still in a layer one spore thick, at the lowest, most dependent portion of the drop. Provided the spore has reached the interface, the attainment of immobility is independent of the direction of its long axis relatively to the surface film. The comparatively few spores which do not settle into close approximation to the air-water interface continue to show Brownian movement.

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* 'Brit. Med. Journ.,' November 9, 1912, p. 1305.

Hanging-drop preparations were also made with particles, of roughly equal size, of carbon, mastic, sulphur, barium sulphate, *Staphylococcus aureus*, etc. All these particles remained in free Brownian movement right down to the bottom of the drop, *i.e.*, they were not affected by the air-water interface.

The formation of the immobile layer was expedited by heat, either by making a hanging drop with nearly boiling water, or by heating after the drop was made; this is probably because of the lessened viscosity, and to a smaller extent the diminished density of the hot water, which permit the spores to gravitate more quickly to the air-water interface.

Spores are bodies of considerable density (about 1·3 grm. per cubic centimetre) but this cannot explain their immobility, several of the other substances used being much denser, *e.g.*, sulphur and barium sulphate. To definitely show that their weight played no part in the immobility at the bottom of the drop, an inverted drop was examined—that is, a drop placed on the microscope slide itself, protected from draughts and evaporation by a cover-slip resting on a vaseline ring without touching the drop. The film of immobile spores was again found at the air-water interface, this time at the top of the drop. This observation is again alluded to below.

Nor is the immobility a result of agglutination; although in densely populated suspensions the spores of the immobile layer are close together, especially about the centre of the surface, they show not the slightest signs of agglutination, either in two or three dimensions. Sparse suspensions were made in which only a few spores appeared in the field of view, and these spores showed the characteristic immobility as soon as they reached the air-water interface, without any attempt at aggregation.

IV. It appeared then that the peculiar behaviour of spores might be due to a surface tension effect, that the spores were in some way able to become part of the surface of the hanging drop, exchanging their kinetic energy of Brownian movement for the potential energy of the surface film.

The cover-slip of a hanging-drop preparation of anthrax spores in which immobility had occurred was lifted, placed on a vaseline ring on a flat slide, and pressed down until the drop came into contact with the glass of the slide. The suspension, now contained between glass surfaces both above and below, was at once examined, and it was found that all the spores exhibited Brownian movement.

Spores in such enclosed-drop preparations are still found chiefly in the lowest portions of the drop, their numbers decreasing rapidly from below upwards, as in Perrin's suspensions of resin particles. But, although the populated region is thus shallow, by reason of the high density of spores as compared with the fluid, it was in no sense a plane, or a surface such as that seen in the immobile layer of a hanging-drop preparation.

Thus, in a suspension of anthrax spores bounded above and below by glass, the distribution usual in suspensions is found—the number of spores in a given horizontal stratum is statistically constant. But if the medium below is air, then the spores close to the air surface become immobile, and a further supply of spores comes down, to be in turn brought to rest. The process continues until practically all the spores have collected into an immobile layer, one spore thick, at the bottom of the drop. Even after a considerable lapse of time, however, a few spores remain in suspension, and consequently continue to show Brownian movement. This does not indicate that they are of a different nature from the immobile spores: that a few spores should remain free for very long periods is to be expected from theoretical considerations. The complete mathematical solution of the state of the suspension, after the lapse of any given time from the moment of formation of the drop, is a difficult matter, depending as it does upon the initial distribution of spores and upon the rate of immobilisation as compared with the rate of settling under gravity; but the problem may be simplified by making the assumptions: (1) that the suspension is initially in the state of statistical equilibrium represented by Perrin's formula in §I above, and (2) that the rate of immobilisation is so slow that it does not disturb this form of distribution of the spores remaining in suspension at any instant. These two assumptions practically amount to the one, that the suspension must have time to settle into the state described in the equation before any large proportion of the spores has been brought to rest. This appears to be very approximately true: at all times throughout the process of immobilisation, as long as any considerable number of spores remain in the body of the liquid, the population in the field of view is observed to grow less and less dense as the microscope tube is raised.

Let $n_0\,dx$ be the number of spores at any instant in a column of unit cross-section and depth dx, immediately above the air-water interface, $n\,dx$ those in a similar layer at a height x above, then $n = n_0e^{-kx}$, where k is a constant.

Hence if s is the total number of spores in the whole vertical unit column,

$$s = \int_0^\infty n\,dx = \frac{n_0}{k}.$$

The rate of immobilisation at the foot of the column at the instant considered is clearly given by the expression cn_0, where c is a constant. Hence $ds/dt = -cn_0 = -cks$, which therefore gives $s = Se^{-ckt}$, where S is the total number of spores in the column initially. Thus the number of spores remaining in suspension only becomes zero after an infinite lapse of time · the observation that some few spores still remain in the body of the fluid and retain their Brownian movement for a long period is thus accounted for

If an immobile layer contains so many spores as to leave no free air-water interface whatever, the upper side of the spore layer acts just as glass would do in an enclosed-drop preparation, with the result that Brownian movement persists indefinitely among the spores compelled to remain in suspension.

V. The immobility of a spore is not produced until it reaches a distance from the air-water interface too small to be measured. If the microscope is focussed on the lowest part of a hanging drop while the process of settling is going on, spores can be observed in all stages from free Brownian movement to complete immobility. On limiting the depth of field in focus by increasing the diameter of the illuminating beam it can always be demonstrated that the most freely moving particles are the highest, and the quite stationary ones the lowest, but the whole depth through which the transition occurs is certainly a small fraction of 1 μ. This would of course be expected if the phenomenon of immobility is a result of surface tension, since Lord Rayleigh and others have shown that the effective thickness of surface films is of the order of a few micromillimetres.

When the upper surface of the drop was the one exposed to air the immobile layer was found to exist from the first at the air-water interface. The greater number of spores gravitated to the bottom of the drop and formed there a population exactly like that of an enclosed-drop preparation, Brownian movement continuing indefinitely. The upper layer of spores, *i.e.* those at the air-water interface, did not fall through the drop but remained immobile. These spores were not, of course, further recruited from the main body of the drop, and were evidently those which happened to be at the interface when the drop was prepared. The immobile spores immediately acquired Brownian movement when the cover-slip was pressed down into contact with the drop, producing an enclosed drop.

In repeating this observation it happened that at a certain part of the margin of the enclosed drop the preparation extended under the cover-slip for a short distance so as to prolong the attachment of the suspending fluid to the cover-slip as compared with the usual more or less abrupt limit of the drop. In this way there was produced a kind of mixed drop, the extension under the cover-slip being of the nature of a shallow hanging drop, the rest of the preparation an enclosed drop. The usual layer of motionless spores appeared at the bottom of the shallow hanging drop; that these spores were not dried on to the cover-glass was shown by the fact that a few free spores were seen moving above them. It was observed that the layer of immobile spores followed the downward curve of the meniscus bounding the main enclosed drop; immediately within that drop, just above the glass of the slide, the spores of the lower layer exhibited the usual Brownian movement of enclosed drops. It was further possible to see the air-water interface edgewise, half way down the meniscus at the boundary of the enclosed drop; only those spores which appeared to be in actual contact with the interface were motionless, those which were within the drop retained their movements up to a distance of less than 1 μ from the meniscus. This directly confirms the statement above that the distance from the interface at which spores lose their Brownian movement is exceedingly small.

To remove any doubt as to whether the spores at the air-water interface might be in some sense dry, enclosed drops, in which every spore was in Brownian movement, were separated into two drops by lifting the cover-slip. It was found that the spores which were left at the air-water interfaces of both the drops thus formed were quite immobile, however quickly the preparations were examined.

VI. The immobile spores seem to lie in a veritable surface skin, for even violent stirring of a drop by a platinum loop fails to restore any considerable number to the body of the liquid. A hanging drop, which was stirred while under observation, showed that the skin of spores was dragged about upon the surface of the drop, but not broken up to any extent. Again, if the microscope stage be tilted through a considerable angle while a hanging-drop preparation is being viewed, the immobile spores merely move slightly with the drop as a whole, while the spores exhibiting Brownian movement in the body of the drop drift rapidly above them across the field.

In some enclosed-drop preparations small air-bubbles occurred; large numbers of spores adhered to their surfaces, and in all cases these spores were absolutely motionless. They were in the fluid, closely attached to the surface of the bubble. Spores in free Brownian movement were noticed at distances less than 1 μ from the bubbles. When by cautious pressure upon the cover-glass a bubble was made to move about, the spores were seen to remain in position upon its surface, rolling with it. Very violent rolling resulted in tearing off the surface film in strips, and the curious appearance was presented of flat tails or ribbons, about 30 μ long and 5 μ broad, composed of immobile spores. These ribbons trailed out from the bubble into the liquid, leaving bare patches of corresponding shape upon the surface of the bubble. The ribbons were presumably held together by minute traces of air, which, being gradually absorbed by the liquid, set free the spores, which broke away one by one to exhibit Brownian movement.

VII. Xylene, paraffin oil, and aniline oil were added to different enclosed-drop preparations of anthrax spores suspended in water. At the interfaces between water and the added liquid, in each case, spores were observed which were quite motionless, whilst those in the water continued their Brownian movement as usual. No spores could be demonstrated within the xylene or paraffin, but the aniline contained a number which were in motion. In certain preparations small drops of xylene were noticed in the water, and their surfaces were studded with immobile spores, just as in the case of the air-bubbles described above. Greasing the slide caused a similar immobility at the bottom of an enclosed drop.

Control preparations of *Staphylococcus aureus* showed none of the peculiarities which we have described—free Brownian movement persisted indefinitely up to the surfaces of air-bubbles, xylene, etc., and in no case was a film of immobile cocci produced.

VIII. The treatment with antiformin alluded to in §II was carefully repeated. Anthrax spores were suspended in 50-per-cent. antiformin and subjected to a temperature of 37° C. for 20 minutes. The suspension was then centrifuged, and the supernatant liquid discarded; the deposit was washed with water and again centrifuged. A suspension of the final deposit was made with water and examined as a hanging drop. The spores were considerably and irregularly reduced in size, and their surfaces appeared to have undergone a corrosive action; the high refractivity usual in spores was now much less marked. In these hanging drops there appeared no trace of the usual immobility, either immediately or after the lapse of days. Occasionally an immobile spore could be found at the air-water interface, but such spores were always large and highly refractile, appearing to have escaped corrosion by the antiformin. The bulk of the particles, as stated, remained in free Brownian movement down to the bottom of the drop, the smallest being, of course, the most active.

A number of untreated spores were added to such a hanging drop, with the result that the immobile layer developed as usual, and was made up of large highly refractile particles, evidently the added spores; the small corroded spores retained their Brownian movement. The continued movement after treatment with antiformin is thus due to an alteration of the surface of the spore, and not to any peculiarity of the liquid resulting from imperfect washing of the centrifuged deposits.

IX. *Summary.*—(1) Bacterial spores examined in hanging-drop and in resting-drop preparations cease their Brownian movement and exhibit immobility at the air-water interface, an immobility involving loss of all Brownian movement even in the plane of the interface. The only subsequent movement is closer aggregation in the interface, due to gravity, as a result of the slope of the surface of the drop.

(2) The immobile spores appear to lie in a veritable skin at the surface of the drop.

(3) Resumption of Brownian movement by immobile spores at the air-water interface can only be induced by (*a*) destruction of the interface by conversion of the hanging or resting drop into an enclosed drop, or partially and with considerable difficulty by violent stirring of the spores at the interface, so as to incorporate them into the body of the drop; (*b*) alteration of the surface of the spores by the action of corrosives.

(4) The phenomenon of immobility is also noted when spores are found at the interface between water and certain "oils," *e.g.*, paraffin, aniline, xylene, and grease.

X. *Discussion.*—The phenomenon of immobility of spores, under the conditions referred to above, indicates a peculiarity in the nature of their surfaces, distinguishing them from other particles of similar size. Since the immobility occurs only at the interfaces between the suspending liquid and other fluids, the effect can be reasonably attributed to surface tension. As the presence of spores at the interface constitutes a final state of stable equilibrium it follows that the attainment of this state is accompanied by a decrease of the potential energy of the system; one way of interpreting this is to suppose that the surface tension is lowered for that portion of the suspending liquid in the immediate vicinity of the immobile spore. On this supposition the phenomenon is closely allied to the increase of concentration in the surface layers of certain solutions, viz., those in which the increase of concentration is accompanied by decrease of surface tension. In such solutions the surface potential energy is reduced by some of the dissolved substance leaving the interior to augment the concentration of the surface film. This excessive surface concentration has been fully discussed by Willard

Gibbs,[*] Sir J. J. Thomson,[†] and others, and has been demonstrated in the froths of solutions of amyl alcohol, sodium oleate, etc., by Miss Benson,[‡] Zawidzki,[§] and Milner.[||] Further, substances have been shown actually to separate out in a more or less solid form from saponin and other solutions and suspensions by Ramsden[¶] and Shorter.[**]

It must be noticed that, while the fact that spores remain at the interface, and are unable to break away from it, may be thus accounted for, no satisfactory explanation is in this way given of the absence of Brownian movement in the plane of the interface; such motion would not require the doing of work against surface forces, and should therefore be possible. The immobility may be due to an abnormally high viscosity in surface films. The existence of such a viscosity has been asserted by many writers: Plateau, Marangoni, and more recently Lord Rayleigh[††] and Shorter (*loc. cit.*) have dealt with the subject. The viscosity may be probably due in some way to a surface contamination; in the present case it is difficult to see how a "clean" surface, in Lord Rayleigh's sense of the term, could be obtained; indeed, the spores themselves may be the "contamination."

Two factors, then, may be regarded as entering into the phenomenon of the immobility of bacterial spores at fluid interfaces · (1) a diminution of surface energy, due to some peculiarity of the spores, this causing them, as soon as they are brought in any way within the range of action of the surface forces, to be drawn into close approximation to the interface; and (2) the abnormal viscosity of surface layers of liquids, which destroys the Brownian movement of the spores. Particles other than spores, not producing a lowering of surface energy, are not drawn into such close contact with the interface, and so do not experience the surface viscosity.

The viscosity concerned must be far greater than that of glycerine, for these layers of immobile spores show not the slightest trace of movement under the highest magnifications, while the Brownian movement of spores in enclosed drops of pure glycerine is readily observable. This, however, is probably not an objection to the hypothesis here put forward. Surface viscosity produces a remarkable effect upon the motions of bodies as relatively vast as magnetic needles and rings of wire, whose inertia is very great as compared with that of spores, and the proportion of the surface exposed to the action of a surface viscosity is also much greater for a spore of dimensions only about 1 μ than for a needle or wire.

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[*] 'Scientific Papers,' 1906, vol. 1, Paper III, "On the Equilibrium of Heterogeneous Substances."

[†] 'Applics. of Dyn. to Phys. and Chem.,' 1888, pp. 190 and 251.

[‡] 'Journ. Phys. Chem.,' 1903, vol. 7, p. 532.

[§] 'Zeit. f. phys. Chem.,' 1900, vol. 35, p. 77; 1903, vol. 42, p. 612.

[||] 'Phil. Mag.,' 1907, vol. 13, p. 96.

[¶] 'Roy. Soc. Proc.,' 1903, vol. 72, p. 156.

[**] 'Phil. Mag.,' 1909, vol. 17, p. 560.

[††] 'Roy. Soc. Proc.,' 1890, vol. 47, p. 281; 1890, vol. 48, p. 127.

There is at present no evidence of an electrical factor in the phenomenon, but further work on this point is in progress.

The Transmission of Cathode Rays through Matter.

By R. Whiddington, M.A., D.Sc., Fellow of St. John's College, Cambridge.

(Communicated by Prof. Sir J. J. Thomson, O.M., F.R.S. Received November 25, 1913,—Read January 29, 1914.)

The experiments of this paper are the outcome of an attempt to discover whether cathode rays are selectively absorbed when their speed is sufficient to excite the radiation characteristic of the material they traverse.

The general laws of absorption of cathode rays were elucidated many years ago by Lenard,[*] and the law which bears his name is expressed by the relation

$$I = I_0 e^{-\lambda x},$$

where I_0 is the "intensity" of a beam of cathode rays incident on an absorbing sheet of thickness x, and I is the "intensity" of the emergent rays. The intensity, as measured by Lenard, was indicated by the brightness of a phosphorescent screen struck by the rays. In the above formula λ is the absorption coefficient. For a definite initial speed of ray λ/ρ is constant, ρ being the density of the absorbing material, while for any material Lenard found that λ varied inversely as the fourth power of the speed of the rays.

In the present experiments the number of the cathode rays incident on and emergent from various metallic sheets is studied.

The general disposition of apparatus is shown in fig. 1, which is not drawn to scale (ebonite insulation is shaded in the diagram).

T is a narrow brass tube passing through an ebonite plug tightly fitting the small brass cylinder C. The top of C consists of the metal leaf under examination, the leaf and the material of C being in close contact. D is another brass cylinder of slightly larger diameter insulated from C by an

[*] Lenard, 'Wied. Ann.,' vol. 56, p. 255 (1895).

ebonite ring. The cylinders C and D were provided with side tubes connected with rubber tubing, so as to prevent the existence of any pressure difference tending to rupture the leaf.

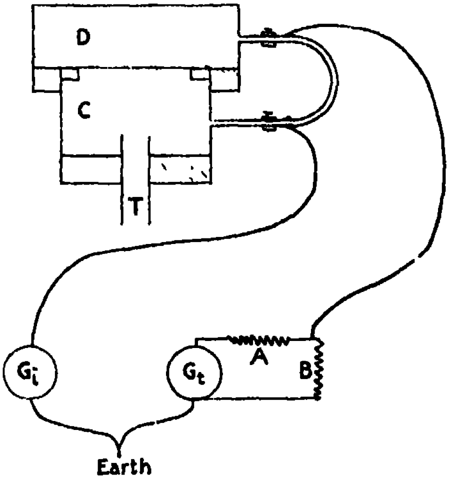

Fig. 1.

Homogeneous cathode rays of known velocity produced by means of a discharge tube and solenoid cylinder* were fired down the tube T.

The rays transmitted by the leaf were measured by the current flowing to earth through the galvanometer G_t, all the transmitted rays being caught by the cylinder D. The rays reflected from and stopped by the leaf were in like manner measured by the galvanometer G_i. These galvanometers were of the moving coil type, the spots of light reflected from their mirrors being focussed on the same scale. It was found that the instrument represented by G_t had to be capable of measuring currents varying between very wide limits, since with slow rays incident on the leaf only a very small number are transmitted, while with fast rays a far greater number are able to penetrate.

For this reason a very sensitive galvanometer was used in conjunction with a shunt of the "Universal" type, indicated by the resistances A and B in the diagram. With this arrangement currents down to 10^{-10} ampère could be conveniently measured.

For the purposes of these experiments only the relative values of the currents i and t registered by the galvanometers G_i and G_t are required. Preliminary experiments were therefore carried out in order to determine the factors, denoted by k in the following equation, by which the actual readings of G_t (with various values of A and B) were to be multiplied to reduce them to the readings which G_6, unshunted, would have yielded with the same current. This was simply done by connecting up both galvanometers in series, passing the same current through both and comparing the readings of the two instruments with various values of A and B.

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* For details of this apparatus see 'Roy. Soc. Proc.,' A, vol. 85, p. 324 (1911).

It was found that k was a function of A and B alone and was independent of the rate of the coil break.

If i and t are the readings of the galvanometers corresponding to the incident and transmitted currents, then of the total current incident on the leaf kt is transmitted. Thus, if the exponential law of absorption is obeyed we must have

$$\frac{kt}{i+kt} = e^{-\lambda x}.$$

The apparatus of fig. 1 is by no means suited to test this law, since it is necessary to take the apparatus down in order to change the thickness of the absorbing leaf. A few preliminary experiments, however, were performed with different thicknesses of absorbing material and cathode rays of a definite speed, and it appeared as if the law were at any rate approximately obeyed. As an example of many experiments to test this point we may take the case of the transmission of cathode rays of velocity about 6×10^9 cm./sec. through two and three sheets of aluminium. In the first case, $\log_{10}[(i+kt)/kt]$ came out 0·918, while in the second case it was 1·568. If the exponential law be obeyed, then the ratio of these logarithms should be the same as the ratio of the leaf thicknesses.

The logarithm ratio is 1·38, while the thickness ratio is 1·5. We may assume, therefore, that the exponential law is roughly obeyed.

Turning now to the main object of the experiments. Measurements of i and t were made with great care, using a definite known thickness of leaf and varying the cathode ray speed over the widest possible limits.

The simplest results were obtained in the case of gold, the results for which are shown graphically in fig. 2.

In this curve the ordinates are proportional to $1/v^4$, while the corresponding abscissæ are proportional to λ, or, what is the same thing, to $\log_{10}[(i+kt)/kt]$. It is clear from this curve that over a considerable range of velocities, λ is proportional to $1/v^4$, or that λv^4 is constant.

Departure from this relation, however, evidently takes place at the point P. Experiment shows that the position of this point depends on the thickness of the absorbing sheet, thicker leaves involving a shift of P down the curve towards the origin. Now, it has been shown in a previous paper[*] that the

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[*] Whiddington, 'Roy. Soc. Proc.,' A, vol. 86, p. 365 (1912).

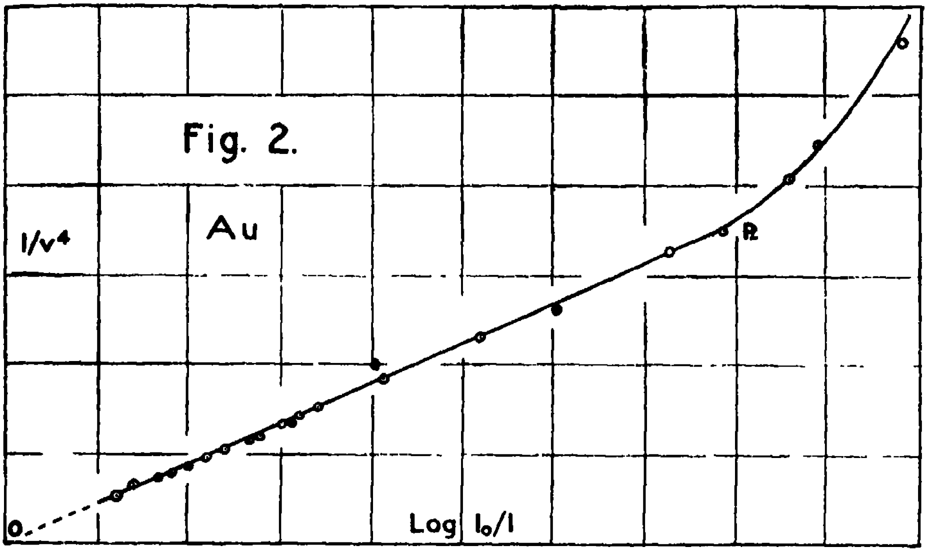

Fig. 2.

loss of velocity of cathode rays in passing through an absorbing material is expressed with considerable accuracy by the relation

$$v_0^4 - v_x^4 = ax,$$

where v_0 = the speed of the rays incident on a sheet of thickness x,
v_x = the speed of the fastest transmitted rays,
a = a constant depending on the material of the sheet.

If in the above formula v_x is put equal to zero, then x will be that thickness of material which can just be traversed by rays of initial speed v_0, or, put in another way, x is the range in the material of cathode rays of speed v_0, the connection between the range and the speed being $v^4 = ax$.

This furnishes an immediate explanation of the point P in fig. 2. The value of the velocity v corresponding to P is connected with the thickness x of the leaf by the above relation, and it is thus possible to deduce from the position of P the value of the constant a.

This constant, calculated from the position of P for very different leaf thicknesses, shows little variation and agrees quite well with the results given in the paper already referred to. A table of results showing the values of a for different materials is given later.

Fig. 3 shows the shape of the $\lambda, 1/v^4$ curve in the case of copper. In this case there is also a linear part in the curve, limited however at both the high- and the low-velocity ends. At the low-velocity end the point P occurs as in the case of gold, and at the high-velocity end there is, in addition, a point of inflection Q. The position of this point does not appear to depend on the thickness of the absorbing leaf, unless, of course, the thickness is so great as to make P approach too near it. After the point R has been passed, the curve again tends to become straight, and, if produced, passes at any rate very nearly through the origin. Thus it is apparent that over the greater part of this curve, over the range of velocities included between the points P and Q, λv^4 is *not* constant.

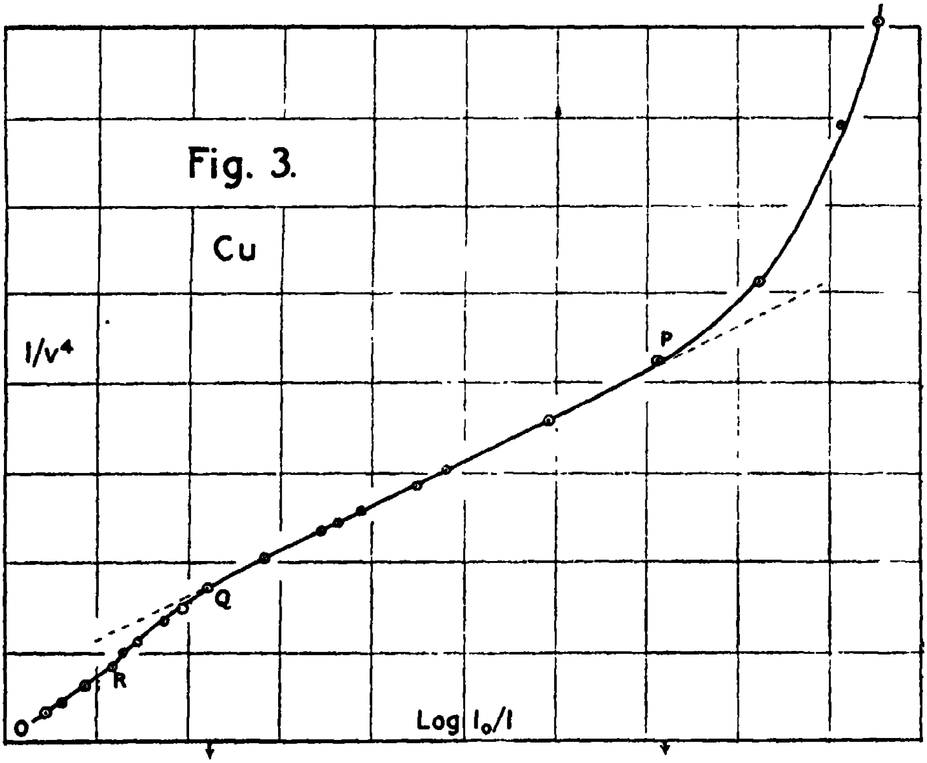
Fig. 3.

It is of interest to notice that the point P corresponds to a velocity of $6{\cdot}2 \times 10^9$ cm./sec., which is almost exactly the speed of cathode ray required to excite the radiation characteristic of copper. The copper type of curve is exhibited by every other metal examined in detail, viz., aluminium, silver, and platinum. Gold stands alone in furnishing a simple straight line passing through the origin. The kink in the curves for the metals other than gold cannot be definitely ascribed to the excitation of the characteristic radiation of the element, since aluminium and platinum both show very well marked kinks in positions which have no very certain connection with the excitation velocity. Considerable trouble was experienced with tin as an absorber. Very irregular results were obtained, it being found quite impossible to repeat observations to any degree of accuracy. It was ultimately noticed that the portion of leaf struck by the rays became extremely thin under the action of the rays, being apparently volatilised; in fact, bombardment by cathode rays in the case of tin would appear to be a convenient method of preparing thin films of this metal.

The equation to the linear part of the curve of figs. 2 and 3 is

$$\lambda = \frac{b}{v^4} + c.$$

The following Table I gives the values of b and c for the metals examined. From this table the value of λ for any speed less than that corresponding to the point Q (v_Q) can be calculated. The last column gives the thickness of leaf experimented with.

Table I.

Absorber.	b.	c.	v_Q.	Leaf thickness in cm.
Al	$4 \cdot 70 \times 10^{43}$	$-20,000$	$6 \cdot 47 \times 10^{9}$	$10 \cdot 4 \times 10^{-5}$
Cu	$7 \cdot 69 \times 10^{43}$	$-27,200$	$6 \cdot 2 \times 10^{9}$	$2 \cdot 23 \times 10^{-5}$
Ag	$11 \cdot 42 \times 10^{43}$	$-5,900$	$>9 \cdot 0 \times 10^{9}$*	$1 \cdot 92 \times 10^{-5}$
Au	$14 \cdot 28 \times 10^{43}$	0	$>9 \cdot 0 \times 10^{9}$	$3 \cdot 25 \times 10^{-5}$
Pt	$10 \cdot 29 \times 10^{43}$	$-4,300$	$5 \cdot 83 \times 10^{9}$	$2 \cdot 04 \times 10^{-5}$

* There is some uncertainty about the value of v_Q for Ag.

Table II gives the values of the constant a calculated from the position of the point P. The last column gives $a/\rho^{\frac{1}{2}}$, which is clearly nearly constant.

Table II.

Absorber.	a.	ρ.	$a/\rho^{\frac{1}{2}}$.
Al	$7 \cdot 3 \times 10^{42}$	$2 \cdot 7$	$4 \cdot 38 \times 10^{42}$
Sn	$14 \cdot 9 \times 10^{42}$	$7 \cdot 4$	$5 \cdot 49 \times 10^{42}$
Cu	$15 \cdot 8 \times 10^{42}$	$8 \cdot 9$	$5 \cdot 4 \times 10^{42}$
Ag	$16 \cdot 9 \times 10^{42}$	$10 \cdot 5$	$5 \cdot 2 \times 10^{42}$
Au	$25 \cdot 4 \times 10^{42}$	$19 \cdot 3$	$5 \cdot 7 \times 10^{42}$
Pt	$28 \cdot 9 \times 10^{42}$	$21 \cdot 5$	$6 \cdot 2 \times 10^{42}$

The relation expressing the change of speed suffered by α-rays in their passage through matter is

$$v_0^3 - v_x^3 = ax,$$

where the symbols have the same significance as in the similar formula for the cathode rays. Now a in this case is proportional to the stopping power of the material for the rays. It follows from this that $a'/A^{\frac{1}{2}}$ is constant,* where A is the atomic weight of the absorbing material. I hope in a future paper to discuss these results and their bearing on some experiments which have been carried out on the absorption of cathode rays in gases.

Summary.

The experiments shortly described in this paper indicate that the law of Lenard stating that the absorption coefficient of cathode rays passing through thin metal sheets is connected with their speed by the relation $\lambda v^4 =$ constant is not generally true when λ is determined from the number of rays incident and transmitted. The alternative formula

$$\lambda = \frac{b}{v^4} + c$$

is shown to represent the facts closely within certain limits of velocity.

It appears that the lower limit of velocity is dependent only on the thickness of the absorbing sheet, while the upper limit is determined by the nature of the metal.

This upper limit in the case of copper screens corresponds exactly to the speed of ray required to excite the Röntgen radiation (K series) characteristic of copper (Curve 3). This is probably a coincidence, as the upper limit in the cases of other metals does not correspond to the excitation of a characteristic radiation. For gold screens the upper limit was not reached, so that for this metal the constant c is zero and therefore Lenard's law is obeyed over a considerable range.

The lower limit of speed provides a ready means of determining the constant a in the relation

$$v_0^4 - v_x^4 = ax,$$

determining the variation in speed of the rays traversing the absorbing sheet. Table II shows the approximate constancy of the ratio $a/\rho^{\frac{1}{2}}$, where ρ is the density of the absorber. In the parallel case of the α-rays the ratio $a'/A^{\frac{1}{2}}$ is constant where A is the atomic weight of the absorber, and $a' = aA/\rho$.

I have pleasure in thanking Prof. Sir J. J. Thomson for his interest in these experiments.

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* $a' = aA/\rho$, a being proportional to the "stopping power" and a' to the "atomic stopping power."

The Variation with Temperature of the Specific Heat of Sodium in the Solid and the Liquid State; also a Determination of its Latent Heat of Fusion.

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Introduction.

The present paper contains the results of an investigation into the variation, with temperature, of the specific heat of sodium in the solid and the liquid state; also, some determinations of its latent heat of fusion.

Our knowledge of the variations of the specific heat of metals in the region of their melting point is extremely vague and hypothetical, since the methods of investigation commonly employed are only capable of giving the mean value of the specific heat over a considerable range of temperature.

In the present work the range of temperature was approximately 1·5° and the series of experiments at a specified temperature give the absolute value of the specific heat at that temperature, without any assumption concerning the value at another point. Further, the use of a small temperature range renders possible determinations of the specific heat at temperatures close to the melting point; in fact, determinations were made with the middle point of the range only 2° below the melting point.

The element sodium was chosen for investigation, on account of its low melting point, as well as the ease with which it could be obtained in quantities and of the requisite purity. It was necessary, however, to devise means of preventing oxidation and this was accomplished by enclosing the sodium in a sheath of copper of special form. This copper case further served as a containing vessel for the sodium when in the molten state.

Construction and Filling of the Case.—The enveloping sheath of copper was so designed that in outline and general dimensions it was similar to the blocks of various metals used in a previous work.*

Several attempts were made before the difficulties of construction were satisfactorily overcome. Molten sodium dissolves soft solder (50 per cent. Sn and Pb), consequently cases with soldered seams failed.

A case was constructed of thick copper foil, the seams of the tubes and case being doubled back and closed. This case was filled with molten sodium, and after solidification the bottom was pressed on and soldered, the solder not coming into actual contact with the sodium.

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* "The Capacity for Heat of Metals at Different Temperatures," by Dr. E. H. Griffiths, F.R.S., and Ezer Griffiths, 'Phil. Trans.,' A, vol. 213, p. 119 (1913).

One series of experiments at 0° were performed with this block and it was then discarded, as the seams were not air-tight and the soldered bottom could not withstand high temperatures.

It is worthy of note that the mean value of the specific heat at 0° from this series, namely, 0·2864, agrees very closely with the value 0·2863 obtained from the second block which was used in all the determinations at the higher temperatures. The results of the individual experiments are given in Table V, p. 571.

In fig. 1 is shown the final design of the copper case together with the apparatus used when filling it.

The exterior walls W were made of two spun copper vessels, the circumferential seam SS being silver soldered. The tubes H and T, which were to contain the heating coil and platinum thermometer respectively, were of solid drawn copper tubing, closed at the lower ends. These tubes were silver soldered to the top of the case. A small tube in the bottom at P enables the case to be filled, and this was finally closed by a screw-on cap.

The weight of the case* complete was 150 grm. and its capacity 386 c.c.

The method of filling this case was to melt the sodium *in vacuo* and force the molten sodium into the case under the pressure of the atmosphere, by slowly admitting air to the exhausted enclosure.

The case was fixed under the bell-jar in the manner shown, the thermometer serving as a guide to keep it vertical. Around the outside of the iron vessel K, containing the sodium, was wound a heating coil of nichrome wire, insulated by asbestos paper, the leads being led out through the base. The interior of the bell-jar was connected to a Geryk pump which was set going for some time before the sodium was melted. Care was taken to ensure an unobstructed passage during exhaustion to the air contained in the case, and the figure represents the conditions prior to melting.

On the sodium attaining the molten state, the case slowly sank by its weight, some of the molten metal entering by the tube P. The heating was continued until the inner tube was at a temperature of at least 20° above the melting point, when the pump was stopped and air slowly admitted.

Molten metal from beneath the oxidised surface was forced into the case and the block was thus composed of sodium practically free from oxide. When the metal had solidified, screwing the small cap on P completed the operation. The sodium used for this block was obtained from Kahlbaum, and the case contained 366 grm.

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* The specific heat of copper and subsidiary substances, together with their variation with temperature, had been previously determined, *loc. cit.*

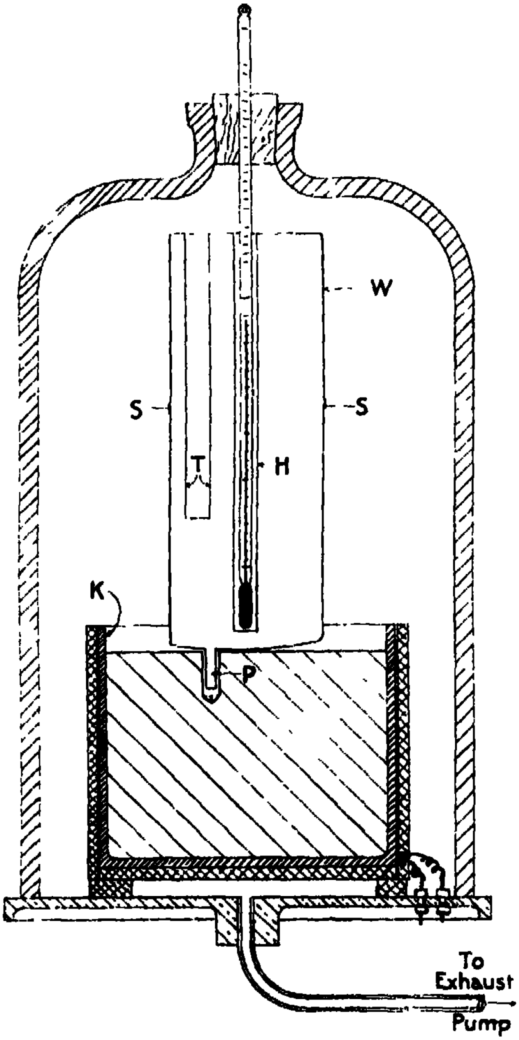

FIG. 1.—Copper case and apparatus for filling.

Determination of the Specific Heat at Various Temperatures.

(a) *Method.*—The method of experiment and the various precautions taken to eliminate sources of error have been described in detail in the paper previously mentioned; here it is only necessary, therefore, to indicate the procedure and the method of reduction, which was practically the same as that previously adopted.

The block was suspended by quartz tubes in an enclosure in a stirred oil tank. The temperature of this tank could be maintained at any desired point for long periods by a controlled electrical heat supply, the oscillations in temperature being of short period and less than 1/50° in magnitude.

An experiment was carried out as follows:—

The block was cooled about 3° below the surroundings, the current was then switched on to the heating coil and adjusted until the potential difference at the ends of the coil was balanced against the E.M.F. of a number of standard cells in series.

When the temperature of the block had risen to about 0·7° below the surroundings, observations of temperature and time were commenced, each transit of the temperature across successive bridge wire divisions (approximately 1/14°) being recorded on a chronograph tape and the observations continued until the temperature had risen to about 0·7° above the surroundings. The time taken to traverse a bridge wire division increased progressively as the temperature rose, on account of the gain or loss due to radiation.

From the data obtained, the values of the rate of rise of temperature, $\partial\theta/\partial t$,* at the corresponding values of θ can be calculated. The value of $\partial\theta/\partial t$ at any point is the sum of two terms: the one due to the electrical supply and the other due to loss or gain by radiation, etc.

When the temperature of the block crosses the surroundings (at θ_N), the loss or gain by radiation vanishes, hence the value of $\partial\theta/\partial t$ at θ_N corresponds to the electrical supply alone, and, having deduced it, the specific heat can be calculated from the well-known expression

$$(ms+\mathrm{MS})\frac{\partial\theta_N}{\partial t}=\frac{n^2\mathrm{E}^2}{\mathrm{JR}f},$$

where $\partial\theta_N/\partial t$ is the value of $\partial\theta/\partial t$ at θ_N, and is calculated from the equation of the straight line representing the relation between the observed values of $\partial\theta/\partial t$ and θ.

The temperature θ is measured relatively to the companion differential thermometer fixed in a duplicate block (contained in a similar enclosure immersed in the tank), the temperature of which is not disturbed during a series of experiments. Thus the position corresponding to θ_N on the bridge wire should be the same at all temperatures of the tank if the arrangement was perfectly symmetrical. Actually, the position of θ_N on the bridge wire varied slightly with the tank temperature, the extreme variation from 30° to

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* Where $\partial\theta$ is the value of 1 bridge wire in ° Pt. at the point and ∂t the time taken to traverse this bridge wire division.

140°, however, only amounted to about 0·03°. At each temperature a series of experiments were performed, in which the rate of energy supply was varied by balancing 4, 5, or 6 standard cells in series.

This variation in the rate of supply affords a severe test of the accuracy of the work, and, moreover, the results of the experiments with different rates afford a means of calculating* the position of θ_N.

To determine θ_N directly requires that the block should have completely settled to the temperature of the surroundings—a process requiring several hours, owing to its asymptotic nature. The calculated position of θ_N generally agreed very closely with the observed value, but where experimental errors at the higher temperatures caused a divergence the observed value was adopted.

The temperature of the tank for each series was determined by a platinum thermometer and reduced to the nitrogen scale.

(b) *Sources of Error.*—In measuring specific heats near the melting point it is necessary to ascertain whether the conditions admit of the fusion of minute portions of the solid by the measured energy supply. An error of this kind would seriously vitiate the results on account of the magnitude of the latent heat of fusion. In the case under consideration, when the electrical supply was on, the inner core of the block around the copper tube containing the heating coil was the region of highest temperature, and a steady gradient existed across the block. An approximate estimate of this gradient can be made by assuming the block to be equivalent to a long cylindrical shell and applying the well-known expression

$$\theta_1 - \theta_2 = \frac{Q \log_e (r_2/r_1)}{2\pi k l},$$

where l, the length of the cylinder, is approximately 15 cm.

r_2, the radius of the outer surface, is approximately 3 cm.

r_1, the radius of the inner surface, is approximately 0·55 cm.

k, the thermal conductivity, is not known, but the value of lead, 0·08 (probably an extreme value), may be taken as a rough approximation.

Q, the rate of energy supply, varied from 0·11 to 0·43 calorie per second.

Hence $\theta_1 - \theta_2$ varied from 0·024° to 0·097°.

Thus, with the heaviest rate of energy supply—that due to a potential difference of 6 Cd cells—the difference in temperature across the block did not exceed one-tenth of a degree.

Apart from this estimate, which involves many assumptions, there is strong internal evidence from the experiments themselves that no perceptible error due to this cause existed, for we should expect that the experiments with the higher rate of supply would be more affected than the slower rate and, consequently, give high values for the specific heat.

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* See 'Phil. Trans.,' 1913, p. 149.

Taking the results of the series with the mid-point of the range 2° below the melting point, we have the following values for the specific heat deduced from the different rates:—

0·3260 from the 4 Cd cell rate.
0·3254 „ 5 „
0·3260 (mean) 6 „

The rate of supply in these experiments was as 16 : 25 : 36. Hence the marked increase in the specific heat (see fig. 2) as the melting point is approached is not due to errors of experiment.

Results.

A remarkable feature of the specific heat values in the solid state is their dependence on the nature of the previous heat-treatment of the metal.

Discrepancies which might at first sight be ascribed to errors of experiment were proved to be of real significance by the fact that the specific heat values in the liquid state could be reproduced to within a few parts in 10,000, after the most varied heat-treatment, while differences of as much as 2 per cent. were encountered in the solid state.

The importance of this point was not sufficiently realised in the early determinations and a large number of otherwise excellent experiments have been rendered worthless through lack of attention to the precise nature of the previous heat-treatment.

It was found that a slow cooling of the block from the liquid state produced an "annealed" condition of the metal in which the specific heat corresponding to each temperature was definite and could be reproduced. A comparison of the dates of the determinations in Table I, which summarises the results for the annealed state, will indicate the extent to which concordant results could be obtained on repetition under similar conditions.

For example, on completing the series of August 8, giving the value 0·2953, the block was taken out, heated up to 100° and allowed to cool rapidly in air. The value then obtained for the specific heat was 0·3014. Again heating to 100°, and allowing to cool very slowly, gave the value 0·2953, identical with the value previously obtained for the "annealed" state at the same temperature. Most of the determinations recorded in Table I correspond to a rate of cooling of the block from the liquid state of certainly less than 4° per hour, which was the rate of fall of the outside tank from 100° to 86°.

Table I.—" Annealed " State.

Temp.	Date.	No. Cd cells.	Specific heat.	Mean.
° 0	Aug. 28...	4	0·2835	0·2829
		5	0·2830	
		6	0·2820	
		6	0·2826	
28·82	Aug 19	4	0·2911	0·2910
		5	0·2910	
		6	0·2929	
		6	0·2893	
49·38	Aug. 8 . .	4	0·2954	0·2953
		4	0·2952	
		5	0·2951	
		5	0·2955	
		6	0·2951	
		6	0·2955	
49·27	Aug. 16	4	0·2946	0·2953
		5	0·2949	
		6	0·2964	
49·07	Aug 17 . Aug 20 . .	5	0·2963	0·2950
		5	0·2945	
		6	0·2942	
67·79	Aug 21	4	0·3014	0·3019
		5	0·3037	
		5	0·3018	
		6	0·3010	
		6	0·3018	
79·15	Aug. 22	4	0·3083	0·3083
		5	0·3085	
		6	0·3086	
		6	0·3079	
85·65	Aug. 15 . . .	4	0·3168	0·3171
		5	0·3181	
		5	0·3165	
		6	0·3178	
		6	0·3159	
90·03	Aug. 23	4	0·3209	0·3209
		5	0·3208	
		6	0·3208	
		6	0·3210	
95·53	Aug. 24	4	0·3260	0·3258
		5	0·3254	
		6	0·3260	

In Table II are summarised the results of a number of determinations of the specific heat after the sodium had been rapidly cooled from the liquid state.

The previous heat-treatment was as follows:—

The block was heated in an oil bath to 130° and then rapidly transferred to a vessel of ice-cold water. This condition of the metal will be termed the "quenched" state in subsequent pages.

The determinations were made starting from the lowest temperature (0° C.) and progressing in steps up to 94°.

It will be observed that the complete series occupied several days and some annealing may have taken place at the higher temperatures. It is now proposed to investigate, by a new method, the changes with time due to slow annealing and also the relationship between crystalline structure and specific heat in the case of other metals besides sodium.

Table II.—"Quenched" State.

Temp.	Date.	No. Cd cells.	Specific heat.	Mean.
0°	Aug. 29	4	0·2892	0·2870
		5	0·2874	
		6	0·2864	
		6	0·2852	
40·16	Aug. 30	4	0·2973	0·2981
		5	0·3002	
		6	0·2953	
		6	0·2992	
		6	0·2983	
68·60	Aug. 31	4	0·3024	0·3040
		5	0·3049	
		6	0·3073	
68·60	Sept. 2	4	0·3034	
		5	0·3320	
		6	0·3038	
82·15	Sept. 3	4	0·3087	0·3089
		5	0·3094	
		6	0·3095	
		6	0·3079	
94·02	Sept. 4	4	0·3195	0·3200
		5	0·3213	
		6	0·3192	
		6	0·3200	

As might be anticipated, the specific heat corresponding to each temperature in the molten state is definite and independent of the previous heat-treatment. The values are collected in Table III. The relation between the specific heat and temperature is practically a linear one over the range of temperature investigated, and it is noteworthy that the temperature coefficient of the specific heat, −0·00034 per degree between 100° and 140°, is very similar to the value for mercury, −0·00030 between 0° and 40°.

The determinations were not done consecutively, the series at 103° being carried out on July 19, while the adjacent series at 101° were done subsequent to a considerable number of determinations (after various heat-treatments) in the solid state, and it is remarkable that the two values 0·3232 and 0·3234 differ by exactly the quantity required for 2° difference in temperature by the coefficient of decrease in specific heat in the molten state. At higher temperatures the experimental errors were more pronounced, and the mean values of several experiments with each rate were taken.

Table III.—Liquid State.

Temp. °	Date.	No Cd cells.	Specific heat	Mean
100·81	Aug. 14 .	4	0·3237	0·3234
		5	0·3226	
		6	0·3227	
		6	0·3246	
103·09	July 19 .	4	0·3232	0·3232
		5	0·3232	
		5	0·3232	
		6	0·3221	
		6	0·3242	
117·03	July 20 . . .	4	0·3218	0·3217
		5	0·3206	
		5	0·3224	
		6	0·3218	
		6	0·3218	
127·53	July 31 and Sept 5 .	4	0·3197	0·3205
		5	0·3205	
		6	0·3212	
138·47	July 30	4	0·3185	0·3189
		4	0·3204	
		5	0·3183	
		5	0·3167	
		6	0·3205	
		6	0·3193	

Fig. 2 represents the results graphically. The relation between the specific heat and temperature in the "annealed" and molten state is shown by the full lines.

The broken line represents the results of the determinations after the sodium had been "quenched." The metal is probably unstable in this state near the melting point, and consequently the specific heat would be a function of time as well as of temperature.

In the early part of this paper reference was made to the fact that experiments were conducted at 0° with two different samples of sodium. As the methods of construction and the quantities involved were different

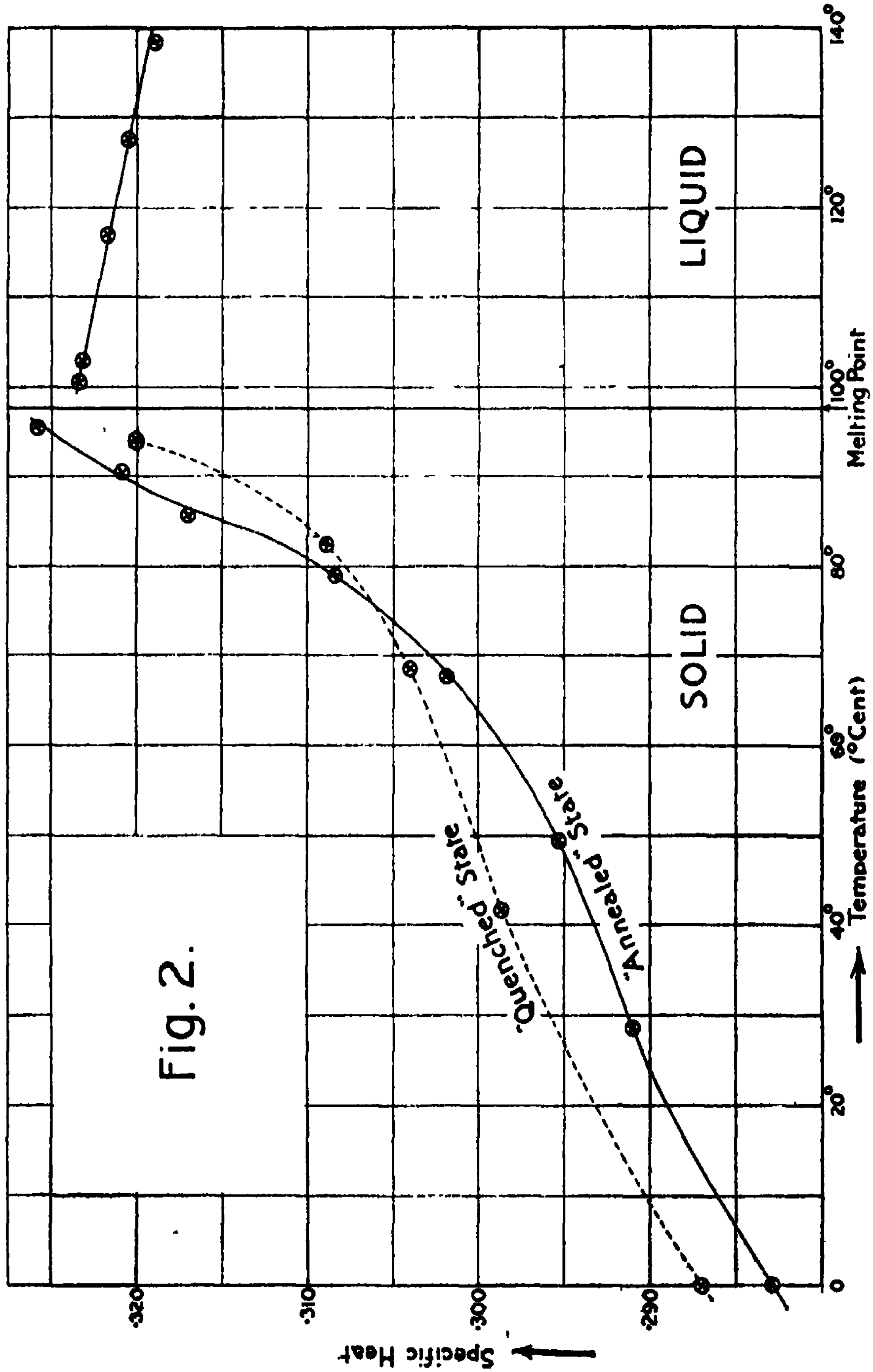

FIG. 2.—The Variation of the Specific Heat of Sodium with Temperature.

in the two cases the results are of importance, inasmuch as they indicate the absence of any serious systematic error. The heat-treatment in both cases was somewhat similar, the sodium being allowed to cool freely in air from the molten state.

Sample A refers to the block constructed with lapped seams and soft solder. This case was filled by pouring in molten sodium from an iron kettle.

Sample B refers to the block constructed from spun copper vessels and filled *in vacuo* with Kahlbaum's sodium.

Table IV.

	Sample A.	Sample B.
Mass of sodium	340·65 grm.	366·04 grm.
,, copper	87·54 ,,	154·3 ,,
,, soft solder	4·37 ,,	
Volume of oil around heating coil	8·08 c.c.	8·5 c.c.
Resistance of heating coil	20·634 ohms	20·028 ohms

The values of the specific heat calculated from the various rates are given in Table V.

Table V.

Sample.	Date.	No. Cd cells.	Specific heat.	Mean.
A	April 7	3	0·2861	
		4	0·2868	
		5	0·2866	0·2864
		5	0·2864	
		6	0·2858	
B	June 4	4	0·2864	
		5	0·2871	
	,, 5	3	0·2862	0·2863
		6	0·2855	
	,, 6	5	0·2864	
		6	0·2863	

The mean value of the specific heat from the above two series is intermediate between the values at 0° for the "annealed" and the "quenched" states respectively (see Tables I and II), and it is noticeable that in both cases the sodium had received heat-treatment of an intermediate character. Several determinations were made at temperatures between 88° and 94° after a somewhat similar heat-treatment, and the same feature is common to all, the values falling between the extremes corresponding to the "annealed" and the "quenched" states. However, in the case of two series at 65° and 81° the values were distinctly higher than those corresponding to the "quenched" state; much weight cannot be attached to these two series, as they were the first performed at the higher temperatures when the thermostat was not working properly.

Determination of the Latent Heat of Fusion.

The following is a brief description of the methods adopted for determining the latent heat of fusion:—The platinum thermometer in the sodium block was disconnected from the differential arrangement used in the specific heat work, and directly connected to a Callendar and Griffiths' resistance bridge. The freezing point was first determined by the cooling curve method, the usual undercooling and superfusion being traced, and the freezing point found to be 97·61° C. The tank temperature was then set and controlled at a temperature of approximately 0·8° below the melting point. The temperature of the sodium block was lowered several degrees below the surroundings, and a heavy rate of electrical supply switched on to the heating coil and maintained constant.

Observations of temperature and time were taken right up to the melting point; near the melting point the rate of rise rapidly decreased to zero. The transition from solid to liquid took from one and a-half to three hours, according to the rate of supply. When the sodium had been converted into the molten state the temperature again rose steadily, and the observations were continued until a sufficient number had been obtained, then the electrical supply was switched off and the cooling curve taken.

From the time-temperature observations in the solid and liquid states it is easy to deduce, graphically or by calculation, the total time required to convert the sodium from solid to liquid, assuming the process to commence and cease sharply at the temperature corresponding to the melting point.

The rate of cooling at various temperatures supplies the data for computing the rate of loss of heat due to radiation, etc., during the time the sodium was melting. Table VI summarises some of the more important data for two experiments done on separate occasions.

A variation of the above method is to determine the total quantity of heat required to raise the temperature of the block from about 90° to 105°.

An experiment by this method, using a 12-cell rate and the surroundings at 96·8°, gave the value 27·7 for the latent heat. The method is not so accurate as the previous one, since the corrections for losses by radiation during the latter part of the experiment become of serious magnitude.

It is interesting to observe that an approximate value of the latent heat can be deduced from the cooling curve alone, without any measurements of energy, provided the thermal capacity of the block and accessories can be calculated from the specific heats.

Table VI.

Mass of sodium = 366·04 grm. Thermal capacity of sodium, case, oil, etc., at these temperatures (calculated from the specific heats) = 143·72 grm.-calories.

	Expt. 1.	Expt. 2.
Number of standard cells balanced	9	12
Resistance of coil for this rate of energy supply*	20·6265	20·6132
Deduced time of melting	10,928 secs.	5,978 secs.
Rate of cooling for this temperature	0·00035° per sec.	0·00033° per sec.
Latent heat	27·54 grm.-cals.	27·50 grm.-cals

* It is to be remembered that at this temperature manganin has a negative temperature coefficient of resistance, hence the heating effect of the current lowers the value of the resistance.

From the time-temperature curve the total time taken to pass from liquid to solid can be deduced. From the observed values of the rate of cooling at various temperatures, the loss of heat per second at the temperature of the melting point can be calculated, and this, together with the thermal capacity at various temperatures, is all that is necessary for an estimation of the latent heat.

But one experiment was made by this method, as the observations were very tedious, the process of solidification alone occupying 6½ hours and the complete experiment necessitated the counting of a tape 800 yards long, with about 29,000 seconds marks.

The duration of the experiment could be shortened by increasing the difference in temperature between the surroundings and the melting point, which in this case amounted to only 8°, but this would render the accurate determination of the rate of cooling at the higher temperatures more difficult.

The value deduced for the latent heat by this method was approximately 27·1 grm.-calories.

The mean value from the first method is undoubtedly the most reliable and the latent heat may be taken as 27·52 grm.-calories.

My thanks are due to Dr. Griffiths, not only for suggestions connected with this inquiry, but also for practical assistance in certain of the experiments, and to my brother, Edgar A. Griffiths, for constructing the cases and for constant help with the observations.

Note.—This investigation must be regarded as an extension of that already published in 'Phil. Trans.,' p. 119, 1913, and as that investigation is now being pursued to lower temperatures, a discussion of the theoretical bearing of the work is deferred until the completion of the low-temperature series.

Note on the Difference in Density between the Annealed and Quenched States of Sodium.

After the preceding paper was written it was suggested that the densities in the two solid states should be ascertained in order to find whether the following generalisation was true :—

That the denser state has the smaller specific heat.

The density determinations here referred to should be regarded as of a preliminary nature only, and the following brief description indicates the method by which they have been obtained.

Two similar spherical glass vessels (with small openings) are suspended in an oil bath from the arms of a short-beam balance.

Both vessels contain sodium, the one annealed and the other quenched, equilibrium being obtained by adding small weights to the lighter side. The annealed specimen is then heated up beyond the melting point and quenched whilst the specimen previously quenched is annealed.

Equilibrium is again obtained, and from the difference in the weights the change in density consequent on change of heat-treatment can be deduced; the cycle of operations being repeated as often as desired.

All the experiments indicate that sodium in the quenched state is *less dense* than in the annealed state ; and further, they consistently indicate that this difference is of the order of 1 part in 7000.

It may be remarked that there is no difficulty in measuring changes of density of this amount by means of the differential method employed; in fact, a difference of one-tenth this magnitude can be measured.

The experimental difficulty is to prevent chemical action between the sodium and any traces of moisture present in the oil.

A point which requires consideration in connection with such minute differences in density is the possibility of the formation of small cavities in the metal when quenching. Cavities filled with the oil under which the manipulations are performed would, however, have no influence on the measurements.

It is of interest to note that if we regard the difference of 1 part in 7000 in the density as being due to the presence of varying amounts of an amorphous modification cementing the crystals together, then the quenched state contains at least 0·3 per cent. more of the amorphous form than the annealed state. This is probably an underestimate, since the value of the density of molten sodium at 98° has been assumed for the amorphous form.—*January* 21, 1914.

The X-ray Spectra given by Crystals of Sulphur and Quartz.

By W. H. Bragg, M.A., F.R.S., Cavendish Professor of Physics in the
University of Leeds.

(Received December 1, 1913,—Read January 29, 1914.)

A number of results of examination of crystals by means of the X-ray spectrometer, which have been recently obtained in this laboratory, are discussed in a paper by W. L. Bragg.* The cases which he has considered are those in which the information has been sufficient for a complete solution of the crystal structure. This note deals with two cases, viz, sulphur and quartz, which have not been completely solved, but which have nevertheless given interesting results.

In one form sulphur is orthorhombic. According to crystallographic measurements of the usual kind it has three unequal axes at right angles to each other, whose lengths are in the ratio 0·813 : 1 : 1·903. It may be assumed at once therefore that the element of structure is based on a rectangular parallelepiped of the form given in the figure. The examination of the spectra given by various planes shows that the assumption is justified.

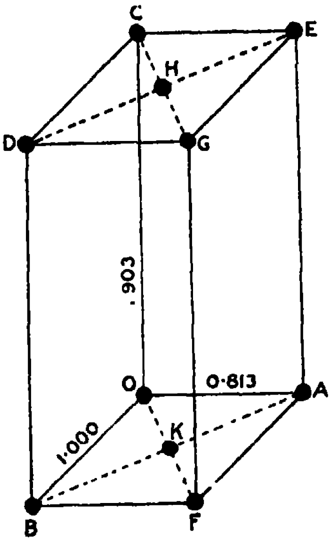

Fig. 1.

It is convenient to say a word at this stage as to the method of preparing crystal planes for examination. Some, of course, occur as natural faces; several of the results given below were obtained from a magnificent sulphur crystal very kindly lent by Prof. Pope. Others it is necessary to cut, but the operation is a very simple one. It is not in the least necessary that the surface should be true or smooth; for the X-rays are reflected by the body of the crystal and not by the surface. It is sufficient to rub down an ordinary sulphur crystal on a piece of sand-paper, judging the result by eye. There would be no need to prepare a surface at all were it not that it is then more convenient to place the crystal correctly in its holder. Some crystals such as spinels, diamonds and rubies cannot of course be cut, and a little calculation is required if they are to be correctly mounted; but if the mounting is difficult, and at first incorrect, the spectrometer readily gives indication as to how it is to be amended.

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* 'Roy. Soc. Proc.,' p. 468 *supra*.

The X-ray bulb which was used in the examination of the sulphur had a palladium anticathode. The principal palladium line ($\lambda = 0{\cdot}576 \times 10^{-8}$ cm.) was reflected by rock salt (100) at the following angles: the references are to fig. 1.

Plane	100	010	001	011	101	110	111
	OCDB	OAEC	OAFB	AODG	BOEG	OCGF	ABC
Glancing angle	6·2°	5·15°	10·5°	5·9°	7° ?	4·07°	4·15°

It is at once clear that there is a connection between these figures and the crystallographic ratios 0·813 : 1 : 1·903. For example, the glancing angles for the planes (100) and (010) are 6·2 and 5·15. These are in the ratio 1 : 0·83; and the spacings of these planes, or rather sets of planes, are therefore in the inverse ratio, or 0·83 : 1. This is very close to the ratio 0·813 : 1. It is to be remembered that the connection between the glancing angle θ, the spacing d and the wave length λ is given by $\lambda = 2\,d \sin\theta$; when θ is small, the sine is of course nearly proportional to the angle itself.

Again the perpendicular from O on the plane ABC is

$$\frac{1}{\sqrt{\left(\frac{1}{a^2}+\frac{1}{b^2}+\frac{1}{c^2}\right)}},$$

where OA $= a$, OB $= b$, OC $= c$.

The value of this expression is easily found to be $b \times 0{\cdot}60$. Now, the glancing angles of the planes (010) and (111) are 5·15 and 4·15, and these are in the inverse ratio of 1 : 1·24, which is very nearly twice the ratio just found.

In the same way the perpendiculars from the origin on the planes AFGE and BCEF are a and $1/\sqrt{(1/b^2+1/c^2)}$; or $b \times 0{\cdot}813$ and $b \times 0{\cdot}885$. These are in the ratio 1 : 1·09. The angles of reflection by the corresponding planes are 6·2 and 5·9. These are in the inverse ratio of 1 : 1·05.

Let us proceed, therefore, to examine the results of assuming the various forms of space lattice which may be associated with this figure (fig. 1). The choice is very limited, and the correct form is readily found to be that in which an atom* of sulphur is placed at each corner of the figure, and at the centres of the two faces perpendicular to the longer axis. Everything (as will presently appear) then falls into place at once, with the exception of the angle of reflection by the (001) plane, an exception which is readily explained. Let us assume this form of lattice and proceed to calculate its dimensions. Two atoms are associated with each element of the lattice shown in fig. 1. Each atom at a corner is at the meeting place of eight volume elements, and one-eighth of it may be said to belong to each element. Hence the whole of these eight count as one. Each of the two atoms at the centres of faces belongs equally to two volume elements having a face in common, and half its value is to be assigned to each element. The two therefore count as one. Summing up, there are two atoms to each unit of volume.

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* It is here assumed that there is one diffracting centre to each atom. This assumption seems to be very clearly in accord with present results.

We have now to find how many interpenetrating lattices there are.

It may be convenient at this stage to explain that the spectra given by a set of interpenetrating lattices are the same as those given by a single lattice if we consider only the positions of the first-order spectra in each case, unless it happens that the planes of one lattice exactly interleave those of the other. To make this clear, let us consider the corresponding case of the diffraction grating. A set of diffracting rulings, A, B, C, D, diffract light of a wave-length at a given angle. If an interpenetrating similar set of lines, A′, B′, C′, D′, is ruled on the same grating parallel to the first, the first-order spectrum occurs in the same place as before, though with altered intensity, unless the second set of lines happens to fall exactly half way between the first, in which case it disappears and the second spectrum becomes the first.

This principle is easily extended to the space lattice. Generally, interpenetrating similarly placed lattices give a first-order spectrum in the same place as any one of the lattices would do alone, unless they are so arranged that they can be derived from one another by movements involving equal successive translations perpendicular to any set of planes, in which case all the spectra given by that set of planes will disappear except the nth, $2n$th, and so on.

If the translations referred to are not equal, the intensities of the spectra of the various orders given by that set of planes will not be the same, either absolutely or relatively to each other, as those given by one lattice; but the position of the first-order spectrum will be the same as if there were only one lattice.

Let us assume that there are n lattices. To every unit of volume abc there are, therefore, $2n$ atoms; for each lattice contributes two. Taking the weight of the H atom as $1{\cdot}64 \times 10^{-24}$, the volume abc contains a mass

$$2n \times 32 \times 1{\cdot}64 \times 10^{-24} \text{ grm.} = n \times 104{\cdot}5 \times 10^{-24}.$$

The density of sulphur is 2·07, and $a = b \times 0{\cdot}813$, $c = b \times 1{\cdot}903$.

Hence $$b^3 \times 0{\cdot}813 \times 1{\cdot}903 \times 2{\cdot}07 = n \times 104{\cdot}5 \times 10^{-24}.$$

$$b^3 = n \times 32{\cdot}75 \times 10^{-24}. \qquad \text{(i)}$$

The glancing angle of the first-order spectrum of the (010) planes is 5·15°, and the spacing of these planes is $b/2$ for the form of lattice we have assumed.

Thus
$$\begin{aligned} 0{\cdot}576 \times 10^{-8} &= b \times \sin 5{\cdot}15^\circ \\ &= b \times 0{\cdot}0898, \\ b &= 6{\cdot}41 \times 10^{-8}, \\ b^3 &= 263{\cdot}4 \times 10^{-24}. \end{aligned} \qquad \text{(ii)}$$

Comparing (i) with (ii) it is clear that n must be equal to 8.

Substituting this value for n in (i) we have—
$$\begin{aligned} b^3 &= 262 \times 10^{-24}, \\ b &= 6{\cdot}40 \times 10^{-8} \text{ cm.} \end{aligned}$$

This gives the actual dimensions of the lattice of fig. 1, and it is now easy to find the relative spacings of the various sets of reflecting planes, and therefore the glancing angles at which the first-order spectra should appear.

The next table compares the values so calculated with those actually observed.

Plane		100	010	001	011	101	110	111
Glancing angle	Calculated...	6·35	5·2	1·33	5·85	6·82	4·06	4·3
	Observed ...	6·2	5·15	10·5	5·9	7·0	4·07	4·15

Except in the case of the (001) plane, the agreement is quite satisfactory. The exception is very interesting; the angle of reflection of the first spectrum is eight times what it should be were there only one lattice. The meaning of this is clearly that the eight lattices are to be derived from each other by movements involving successive equal translations parallel to the c axis; this causes all the spectra to disappear up to the eighth, in the manner explained above.

The spectra given by sulphur are all weak, particularly in the case of the (101) plane, and in no case have any been found so far of higher order than the first. Consequently there are no available data at present for proceeding further with the calculation of the relative positions of the eight lattices.

The analysis of the quartz spectra may be carried out on much the same lines as those of the preceding argument, and a briefer discussion will be sufficient.

The results show, as would be anticipated, that it is necessary to use a hexagonal lattice, as in the figure, where $Ii = c$, $IF = a$, and $c = a \times 1{\cdot}1$, according to crystallographic data.

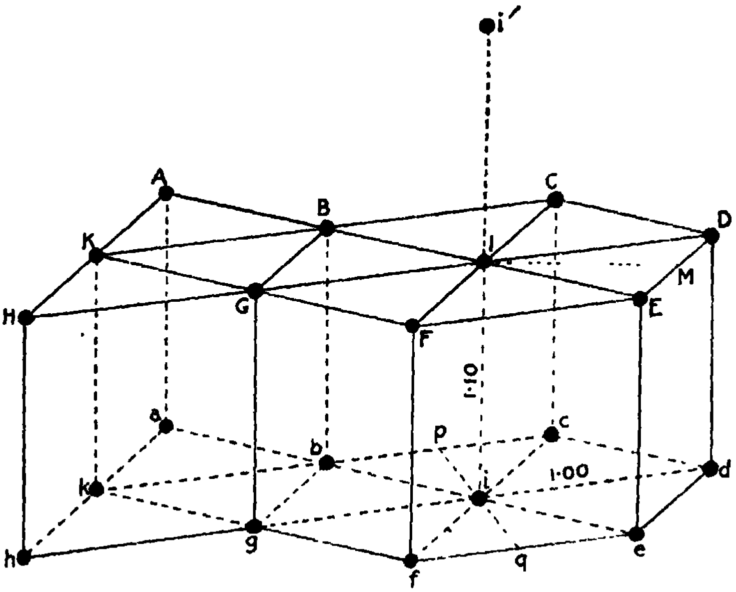

FIG. 2.

The palladium principal ray is reflected by a prism face at a glancing angle 3·90°.

Hence $$\mathrm{IM} = \frac{\lambda}{2\sin\theta} = \frac{0{\cdot}576\times10^{-8}}{2\times0{\cdot}0680} = 4{\cdot}23\times10^{-8}.$$

$$a = \mathrm{IM}\ \mathrm{cosec}\ 60^\circ = 4{\cdot}88\times10^{-8}.$$

We may take IDEF*idef* as the elementary parallelepiped, having an atom at each corner. Its volume

$$= ca^2\sqrt{3}/2 = 111{\cdot}3\times10^{-24},$$

and since the density of quartz is 2·66, the mass associated with it $= 2{\cdot}66\times111{\cdot}3\times10^{-24} = 296\times10^{-24}$.

If n is the number of molecules associated with the parallelepiped, the mass must also be given by

$$n(28{\cdot}3+32)\times1{\cdot}64\times10^{-24} = n\times99\times10^{-24},$$

or the atomic weight of Si and O are 28·3 and 16 respectively, and the mass of the H atom is $1{\cdot}64\times10^{-24}$. The value of n is therefore 3, that is to say, there are three space lattices of the assumed form, with each of which one molecule is associated.

The spacings of the various sets of planes may now be calculated, and thence the angles at which the palladium line should be reflected. These are compared with the observed values in the following table :—

Plane………	ED*de*	I*de*	FD*df*	G*pq*	*i'de*	BG*ed*	AH*ed*	BDF
Observed …	3·9	4·93	6·60	9·2	8·4	7·25	10·15	?
Calculated…	3·9	4·95	6·75	9·1	8·3	7·3	9·5	?

It is curious that so far no reflection has been found from the plane BDF, the plane which is perpendicular to the principal axis.

[*Note added January* 6, 1914.—Since this was written a weak reflection from this face has been found. The value of the glancing angle shows that the spacing of the planes parallel to BDF is one-third of I*i*. This means that the three lattices can be derived from each other successively by movements involving equal translations parallel to the *c* axis. The result was to be expected.]

Many of the planes give very good reflection, and spectra of more than one order, so that it will no doubt be possible to complete the analysis of the quartz structure eventually. So far, it is clear that there are three interpenetrating lattices of the given form for every atom in the molecule. The three must no doubt be arranged as suggested by Groth, so that they can be derived from each other successively by a translation equal to $c/3$ along the c axis accompanied by a rotation of 120° about a line parallel to that axis. This constitutes a screw motion, which may be either right- or left-handed. It remains to complete the determination of the positions of the silicon and the oxygen lattices with reference to the line of rotation.

On Natural Radiation from a Gas.

By **George Green**, D.Sc., Lecturer on Natural Philosophy in the University of Glasgow.

(Communicated by Prof. A. Gray, F.R.S. Received December 1, 1913,—Read January 29, 1914.)

In a paper "On the Character of the Complete Radiation at a given Temperature,"* Lord Rayleigh discusses the possibility of representing complete radiation at any temperature as an aggregation of pulses all of one definite type. The form of pulse assumed in the investigation is that of the error function $\epsilon^{-c^2x^2}$, so that each pulse may be regarded as due to elementary impulses aimed at the same point in space under the law of error, or they may be regarded as distributed in time under the same or a similar law. The pulses themselves are assumed to be similar, but not necessarily equal, and their occurrence is random in the sense that velocity of molecules in a gas is random, that is, their numbers and intensities vary in such a way as to produce effects which are statistically steady. The investigation may be regarded as an attempt to derive the law of complete radiation by means of a summation of impulses such as are supposed to occur at collisions in gases on the kinetic theory. On this view collisions would naturally be regarded as the source of radiation, but it is unnecessary at this point to restrict our ideas regarding the type of fundamental pulse by special assumptions regarding the mechanism of radiation.

Some time later Mr. Charles Godfrey† obtained expressions for the radiation from an incandescent gas, taking the fundamental form of pulse to be a limited train of regular vibrations. The gas is assumed to consist of molecules, with vibrators or electrons, all having the same period of free vibration, and the radiation is taken as a series of regular trains of vibrations emitted by the vibrators in the intervals between the collisions of the molecules. The type of pulse here discussed is chosen as most suitable for determining the influence of the various lengths of free path of molecules, and of motion of molecules in the line of sight, in tending to produce broadening of the spectrum lines of the gas. The energy emitted by molecules of speed v, in the range of frequency n to $n+dn$, is first obtained, and an integration over the various velocities then gives the total energy in the region of the spectrum considered. Thus the total radiation of the gas is not in question in this paper, or in the note regarding it by Lord Rayleigh* in 'Proc. Roy. Soc.,' vol. 76, 1905, but it is clear that, if we extend the restricted idea of pulse used in this investigation to include disturbances originating at collisions of molecules, as well as regular vibrations emitted between collisions, and carry out the same summation of the probable effects due to the various groups of molecules, we ought to arrive at the law of complete radiation for the gas.

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* 'Phil. Mag.,' 1889, vol. 27.

† "On the Application of Fourier's Double Integrals to Optical Problems," 'Phil. Trans.,' A, vol. 195, p. 329 (1900).

The difficulty of this line of approach to the law of complete radiation is, of course, that the form of the constituent pulses is entirely unknown. It seems to be definitely established, however, from the investigations of Planck, that the total energy radiated from a black body at any temperature is emitted in the form of discrete quanta of energy, all equal and similar. The existence of discrete quanta of energy in the process of emission need not be taken to indicate a molecular structure for energy, but may arise from the constitution of the molecule, which may be such that emission always occurs accompanied by a definite change of constitution or rearrangement of the system, involving the radiation of a definite quantity of energy. In this view we virtually identify the quantum of energy with the energy of a pulse emitted by a molecule of the gas, and the problem becomes to determine the form of this pulse, so that a proper summation of similar pulses leads to Planck's law of radiation. The form of this pulse might convey some indication of the mechanism of radiation in any black body.

At first sight it seems as if the form of pulse, with the same distribution of energy per wave-length at a given temperature as stated in Planck's law of radiation, is all that is required. But this is not so, for the form and energy content of the pulse would in this case vary with the temperature while the quantum is understood to be a constant. If we identify the quantum of energy with the energy of similar elementary pulses, a sequence of which constitutes total radiation, we must assume that their number and distribution in space changes with the temperature.

The aim of the present investigation is to derive a form of pulse in agreement with Planck's law of radiation at any temperature and to discover if any information can be obtained regarding the constitution of natural radiation by decomposing this pulse. The form of pulse which gives the same energy per wave-length as required by Wien's law has recently been communicated to the Royal Society by Dr. R. A. Houstoun,† but as the required form for agreement with Planck's law has been now derived by direct investigation I shall indicate the process by which it has been obtained.

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* "On the Influence of Collisions and of the Motion of Molecules in the Line of Sight upon the Constitution of a Spectrum Line."

† "The Mathematical Representation of a Light Pulse," this volume, p. 399.

Consider the distribution of radiant energy per wave-length due to a single impulse delivered at the origin at time $t = 0$. It is proved below that the energy per wave-length is the same in the unresolved form of the pulse as when resolved by Fourier's theorem, or by any dispersive medium. For convenience, therefore, we may take the case of an impulse in a dispersive medium, in which V is the velocity of an infinite train of waves of wave-length λ, and period $2\pi/k\mathrm{V}$, where $k=2\pi/\lambda$, and $\mathrm{V}=f(k)$. This makes available the solution for the effect of an impulse given by Lord Kelvin in his paper of 1887,[*] "On the Waves produced by a Single Impulse in Water of Any Depth, or in a Dispersive Medium." From that paper we find, for the displacement ξ, at point x, at time t, the expression

$$\xi = \frac{1}{2\pi}\int_0^\infty dk \cos\left[k\left\{x-tf(k)\right\}\right]$$

$$= \frac{\cos\left[k\left\{x-tf(k)\right\} \pm \frac{1}{4}\pi\right]}{\sqrt{\left[\mp 2\pi t\left\{2f'(k)+kf''(k)\right\}\right]}} = \mathrm{A}\cos\theta. \tag{1}$$

In this k corresponds to the wave-length λ of the group of Fourier trains which predominate at point x, at time t; and the sign is to be chosen in the denominator to make the expression positive. The value of ξ obtained is for t great, and x correspondingly great. The condition that wave-length λ predominates at point x at time t is that

$$x = \left\{f(k)+kf'(k)\right\} t = \mathrm{U}t, \tag{2}$$

where U is the group-velocity corresponding to wave-length λ; and the extent of the medium from the plane where wave-length λ predominates to the plane where wave-length $\lambda+d\lambda$ predominates, at time t, is therefore

$$dx = t\left\{2f'(k)+kf''(k)\right\} dk, \quad \left(dk = -\frac{2\pi}{\lambda^2}d\lambda\right). \tag{3}$$

Since energy of wave motion per unit length of the medium is proportional to the square of the amplitude, the above expressions show that the energy of the disturbance in the range of wave-lengths from λ to $\lambda+d\lambda$ is proportional to dk: or, if we express this result in the notation commonly employed in optics, we obtain

$$\mathrm{E}\,d\lambda = \frac{c}{\lambda^2}d\lambda, \tag{4}$$

where c is a constant.

This is the result referred to above, namely that the energy associated with any range of wave-lengths $d\lambda$ depends only on the wave-lengths concerned, being the same at all stages of the process of dispersion as in the unresolved pulse. It is true for any form of initial pulse provided we substitute an arbitrary function, $\phi(\lambda)$, for c/λ^2. Thus the energy per wave-length contained in the part of any wave disturbance in a dispersive medium, where the wave-length is λ, is a constant determined by the form of the initial disturbance alone. Since the wave-disturbance of wave-length λ moves with the corresponding group-velocity we see that the group-velocity determines the rate of flow of energy at each point of the medium—a theorem first stated by Lord Rayleigh for an extended group of waves.*

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[*] 'Roy. Soc. Proc.,' vol. 42.

Consider now the distribution of energy per wave-length when the initial disturbance is a pulse of any given form. In this case let

$$\xi = \mathrm{F}(x), \qquad \frac{d\xi}{dt} = 0, \tag{5}$$

represent initial conditions. $\mathrm{F}(x)$ is understood to be practically limited to a region close to the origin on either side. According to the Fourier synthesis the displacement at point x at any later time is

$$\xi = \frac{1}{2\pi}\int_{-\infty}^{\infty} dx_1 \mathrm{F}(x_1) \int_0^{\infty} dk \cos\left[k\left\{(x-x_1)-tf(k)\right\}\right]. \tag{6}$$

The most important terms of this expression have been given in a paper by the present writer in 'Proc. Roy. Soc. Edin.,' 1909–10.† When Lord Kelvin's value of the first integral is inserted in the above, it is found that, for places very distant from the origin and for all the time in which the displacement is comparable to the first order with its maximum value, the value of ξ is

$$\xi = \mathrm{A}\cos\theta\int_{-\infty}^{+\infty} dx_1 \mathrm{F}(x_1)\cos kx_1 + \mathrm{A}\sin\theta\int_{-\infty}^{+\infty} dx_1 \mathrm{F}(x_1)\sin kx_1, \tag{7}$$

where A and θ are taken from equation (1) above. We might choose $\mathrm{F}(x)$ either as an even or as an odd function, and in any case it is convenient to distinguish the two types of initial pulse, namely, those satisfying the equation $\mathrm{F}(x) = \mathrm{F}(-x)$ and those for which $\mathrm{F}(x) = -\mathrm{F}(-x)$. For the even type, by an application of the process applied above to the single impulse, we obtain, for the energy associated with the range of wave-lengths λ to $\lambda + d\lambda$, the expression

$$\mathrm{E}\,d\lambda = \frac{c\,d\lambda}{\lambda^2}\left[\int_{-\infty}^{+\infty} dx_1 \mathrm{F}(x_1)\cos kx_1\right]^2; \tag{8}$$

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* 'Theory of Sound,' vol. 1, Appendix.

† "On Waves in a Dispersive Medium resulting from a Limited Initial Disturbance."

and for the odd type we find

$$\mathrm{E}\,d\lambda = \frac{c\,d\lambda}{\lambda^2}\left[\int_{\infty}^{+\infty} dx_1 \mathrm{F}(x_1)\sin kx_1\right]^2. \tag{9}$$

The value of E which is required in either case for Planck's law is

$$\mathrm{E} = \frac{c_1}{\lambda^5}\cdot\frac{1}{e^{c_2/\lambda\mathrm{T}}-1}, \tag{10}$$

so that the condition to be fulfilled by $\mathrm{F}(x)$ is contained in the equation

$$\int_{-\infty}^{+\infty} dx_1 \mathrm{F}(x_1)\begin{array}{c}\cos kx_1\\ \sin kx_1\end{array} = \lambda^{-3/2}e^{-c_2/2\lambda\mathrm{T}}\left(1-e^{-c_2/\lambda\mathrm{T}}\right)^{-\frac{1}{2}}$$

$$= \sum_{n=0}^{n=\infty}\frac{1.3.5\ldots(2n-1)}{2.4.6\ldots(2n)}\lambda^{-3/2}e^{-\frac{1}{2}(2n+1)c_2/\lambda\mathrm{T}}, \tag{11}$$

unity being coefficient of the term $n = 0$.

Each term on the right is of the form $k^{3/2}e^{-\alpha k}$. Express this in the form of a Fourier double integral

$$k^{3/2}e^{-\alpha k} = \frac{1}{\pi}\int_0^\infty dx\int_0^\infty dz\, z^{3/2}e^{-\alpha z}\cos x\,(k-z), \tag{12}$$

and perform the integration with respect to z. The result is

$$k^{3/2}e^{-\alpha k} = \frac{\Gamma(\frac{5}{2})}{\pi}\left[\int_0^\infty dx\,\frac{\cos\frac{5}{2}\theta}{(\alpha^2+x^2)^{5/4}}\cos kx + \int_0^\infty dx\,\frac{\sin\frac{5}{2}\theta}{(\alpha^2+x^2)^{5/4}}\sin kx\right], \tag{13}$$

where $\theta = \tan^{-1}(x/\alpha)$. It is unnecessary at present to find the values of these integrals separately, inasmuch as they can be derived by realising the complex expressions

$$\int_0^\infty dx\,\frac{\cos kx}{(\alpha+\iota x)^{5/2}} \quad\text{and}\quad \int_0^\infty dx\,\frac{\sin kx}{(\alpha+\iota x)^{5/2}},$$

and it is thus clear that the even function required for agreement with any term of Planck's expression is

$$\xi(\alpha,x) = \frac{\cos\frac{5}{2}\theta}{(\alpha^2+x^2)^{5/4}},$$

and the odd function is

$$\xi(\alpha,x) = \frac{\sin\frac{5}{2}\theta}{(\alpha^2+x^2)^{5/4}}, \tag{14}$$

with $\theta = \tan^{-1}(x/\alpha)$.

The complete expression for a pulse with energy per wave-length as in Planck's law is, omitting constant multipliers,

$$\xi(\alpha,x)+\tfrac{1}{2}\xi(3\alpha,x)+\ldots+\frac{1.3.5\ldots(2n-1)}{2.4.6\ldots2n}\xi\{(2n+1)\alpha,x\}+\text{etc.}; \tag{14$'$}$$

or as we may write it to show more clearly how it depends on T, the absolute temperature,

$$\sum_{n=0}^{n=\infty} \frac{1.3.5\ldots(2n-1)}{2.4.6\ldots 2n} \cdot \frac{1}{(2n+1)^{5/2}} \xi\left(\frac{c_2}{2\mathrm{T}}, \frac{x}{(2n+1)}\right).$$

A diagram of the form $\xi(\alpha, x)$ has been given in Dr. Houstoun's paper referred to above.

In applying results obtained above to a gas we must obviously suppose the radiation from the gas to be restricted to the direction of x. Also, as it may appear artificial to represent the aggregate radiation by a displacement form extending throughout space, it is important to remark that the constituent pulses which we have assumed might equally well have been taken as distributed in time according to a similar law so as to give the same aggregate effect.

Let us now consider how the above pulse may be decomposed into constituents of some simpler form. This may be possible in several ways, but if we take the terms similar to $\xi(c_2/2\mathrm{T}, x/(2n+1))$ and express each as an integral in the manner indicated below, the results admit of simple interpretation belonging to the kinetic theory of gases. Thus we can write, as in (12) and (13) above, for the even function,

$$\xi(\alpha, x) = \frac{\cos\frac{5}{2}\theta}{(\alpha^2+x^2)^{5/4}} = \frac{1}{\Gamma(\frac{5}{2})}\int_0^\infty e^{-\alpha z} z^{3/2} \cos xz\, dz, \tag{15}$$

and if we replace z in this expression by v^2 we obtain

$$\xi(\alpha, x) = \frac{2}{\Gamma(\frac{5}{2})}\int_0^\infty e^{-\alpha v^2} v^4 \cos xv^2\, dv. \tag{16}$$

The meaning of this is that the composite pulse obtained in (14′) above may be regarded as the aggregate effect of simple wave-trains emitted by the various groups of molecules in the gas obtained by arranging the total number according to speed at any temperature. In the single term considered in (16) the effect due to molecules whose speed lies between v and $v+dv$ is evidently proportional to $e^{-\alpha v^2} v^4 \cos xv^2 dv$. The value of α is $c_2/2\mathrm{T}$, where c_2 is taken from Planck's formula, and we have therefore (by introducing a suitable constant with v^2 in (15) above) $e^{-\alpha v^2} v^2 dv$ proportional to the number of molecules whose speeds lie between v and $v+dv$ at any temperature. Thus the displacement form which represents the contribution to the total radiation made by the n molecules in the group $(v, v+dv)$, at any temperature, is given by

$$\xi = v^4 \cos xv^2\,dv \left\{ e^{-av^2} + \frac{1}{2} e^{-3av^2} + \frac{3}{8} e^{-5av^2} + \ldots + \frac{1.3.5\ldots(2n-1)}{2.4.6\ldots 2n} e^{-(2n+1)av^2} + \text{etc.} \right\}$$

$$= \frac{e^{-av^2} v^4\,dv}{(1-e^{-2av^2})^{\frac{1}{2}}} \cos xv^2. \tag{17}$$

We have thus arrived at a form of pulse which represents complete radiation at all temperatures, and the statistical relation between it and the harmonic constituents of the radiation emitted by the various groups of molecules. Meantime fuller discussion of the above is reserved for a later paper.

On the Temperature Variation of the Photo-elastic Effect in Strained Glass.

By L. N. G. Filon, M.A., D.Sc., F.R.S., Goldsmid Professor of Applied Mathematics and Mechanics in the University of London.

(Received December 30, 1913,—Read January 29, 1914.)

1. The object of this investigation was to determine in what manner the stress-optical coefficients of glass vary with change of temperature. The method of measuring the stress-optical coefficients was the one described in 'Proc. Roy. Soc.,' A, vol. 83, pp. 573 *et seq.*, but the following modifications were introduced for the special purpose in view.

2. The glass slabs were enclosed in a double-walled copper chamber. In the space between the two walls a constant circulation of steam could be maintained. Two windows of plane parallel glass in the front and back of the chamber allowed light, previously analysed by a grating, to traverse the slabs and to be focussed in a spectrographic camera.

The plan and front elevation of the chamber are shown in fig. 1

Apertures were provided in the sides of the chamber to allow long wooden arms, by means of which bending moment without shear could be applied to the slabs, to project outside. As a certain amount of free play had to be allowed to these arms, the apertures could not be made close-fitting or packed tightly with cotton wool. In order to prevent draughts and loss of heat, thick felt pads P_1, P_1', P_2, P_2', were fitted round the arms at the exit and entrance to the apertures as shown in fig. 1. This practically closed the apertures while allowing the arms free motion, and the friction of the pads could be neglected in comparison with the other forces applied.

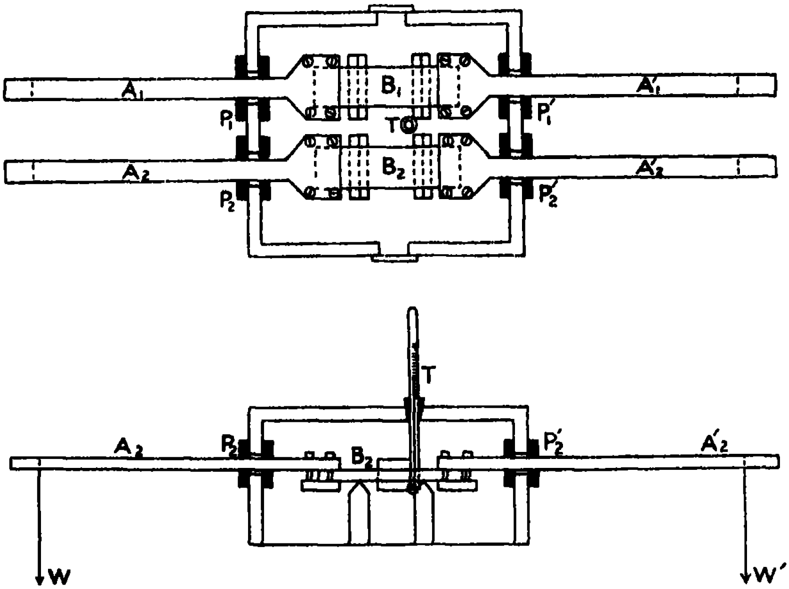

Fig. 1.

An arrangement of partitions (not shown in the figure) inside the double wall ensured that steam circulated evenly through every part of the hollow wall.

A thermometer T passed through a cork in the roof of the chamber, its bulb being between the two slabs just outside the path of the rays of light. When a steady state had been reached inside the chamber, the reading of this thermometer was assumed to give the temperature of the glass slabs.

Under the circumstances it was impossible to avoid a fairly large loss of heat through the various apertures. Nevertheless a steady temperature of 91° to 94° C. was always attained, and the definition of the spectrum after passing through the slabs showed that there can have been no serious inequalities of temperature inside them.

3. The correction for the prismatic shape of the slabs induced by flexure was allowed for, as explained in the paper referred to, by immersing the slabs between two layers of oil. The use of oil of cedarwood, which was employed previously, had to be discontinued, as it was found to coagulate at the higher temperatures. A sample of transformer oil, for which I am indebted to the kindness of the Vacuum Oil Company, Ltd., was used instead, and so far has proved entirely satisfactory. The index of refraction of this oil had to be determined at both temperatures. This was done by measuring photographically the deflection of a spectrum line after traversing a wedge

cell, whose faces were of optically worked glass, filled with the fluid whose refractive index was required. The angle of the wedge was first found by measuring the deflection produced when it was filled with water at ordinary temperature. It was then filled with oil, placed inside the double-walled chamber, and the deflection was again measured at any required temperature. The index of refraction of the oil for the given line of the spectrum could then be calculated.

4. A precisely similar method was used to determine the normal index of refraction of the glass used, when unstressed, at the temperatures of the experiments. Previously this refractive index had been obtained by fitting the usual dispersion formula to the values of the refractive index for a few standard lines, as supplied by the makers.

This method had long been felt to be unsatisfactory, and for the higher temperatures it was unavailable. Accordingly prisms of small angle were cut from the material of the slabs and the deflections of every spectrum line used read off at the lower and higher temperatures. The refractive indices were then calculated.

5. The glasses used were Jena glasses, transparent to ultra-violet light and bearing the maker's catalogue number UV 3199. These had already been examined at ordinary temperatures some three years before, and the results published in the paper already quoted.

It was now discovered that a certain amount of anomalous dispersion existed for two wave-lengths in this glass: and that this anomalous dispersion was intensified by rise of temperature. The discussion of this effect, however, it is proposed to reserve for a separate paper. As a matter of fact its influence on the correction for prismatic shape due to bending was found to be very slight; but it may have an important bearing on the interpretation of similar anomalies in the photo-elastic effect.

6. The stress-optical coefficients were calculated by the method described in 'Proc. Roy. Soc.,' A, vol. 83.

The results are expressed in a unit of 10^{-13} cm.^{2} per dyne. In the paper quoted above I used a unit of 10^{-10} cm.^{2} per gramme weight, and proposed to call it a *brewster*. Since then it was pointed out to me that it would be preferable to use in all cases an absolute, instead of a gravitational unit. The new unit is about 1·02 of the old, and I propose to transfer to it the suggested name of *brewster*.

The values of the stress-optical coefficients C_1, C_2* (both of which are negative), are given in columns II, III, V, VI of the table below for temperatures of 18° C. and 90° C. In columns I and IV have been entered the values of C_1, C_2 as determined for the same glass at about 15° C. some three years previously. These are taken from Table II of the paper quoted above, but expressed in the new units.

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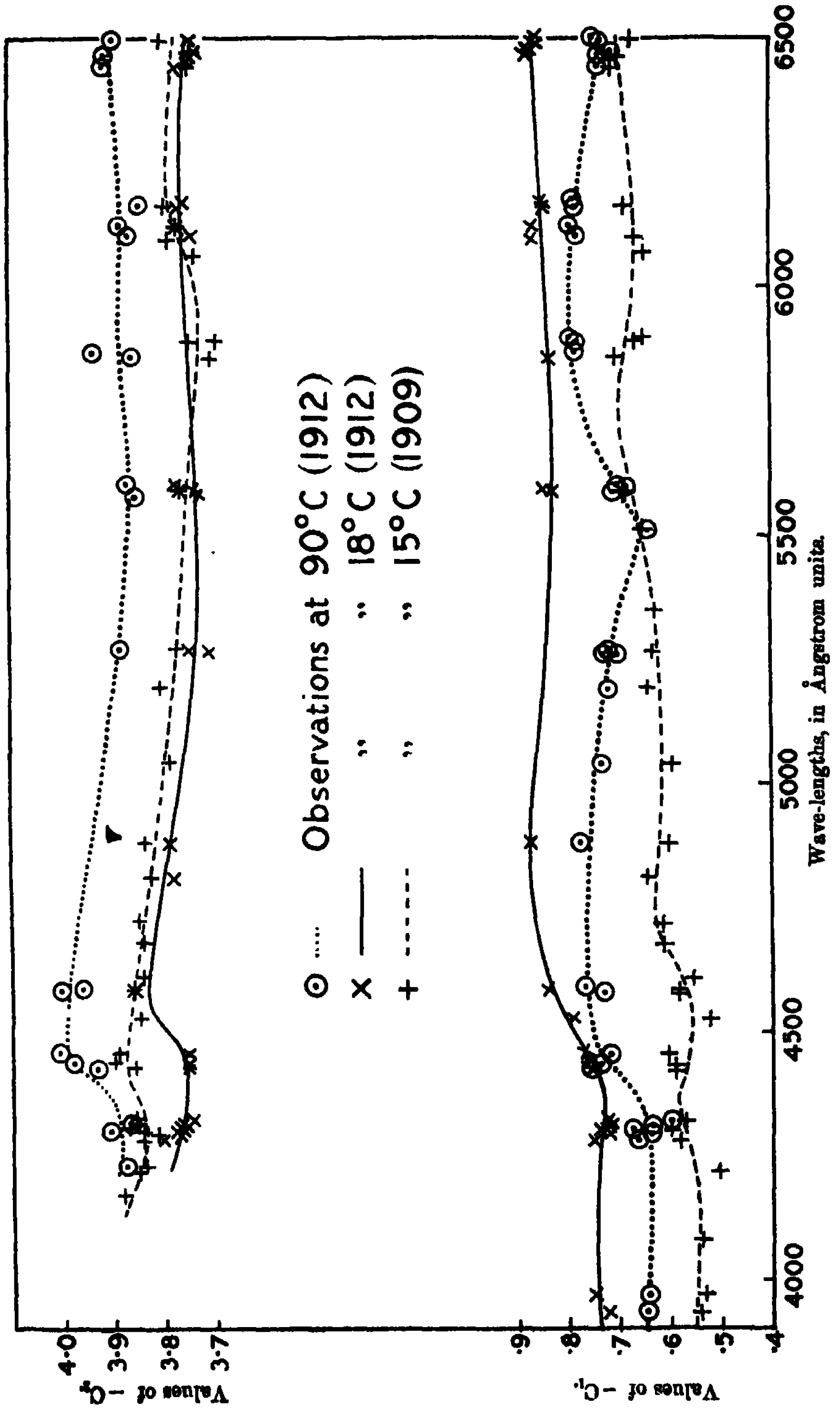
* C_1 is defined as the increase per unit tension of the index of refraction of the ray polarised in the line of stress; C_2 as the corresponding quantity for the ray polarised perpendicularly to the line of stress.

Table of Stress-Optical Coefficients for Glass UV 3199.

λ.	I. $-C_1$. At 15° C. (1909).	II $-C_1$. At 18° C. (1912).	III. $-C_1$. At 90° C. (1912).	IV. $-C_2$. At 15° C. (1909).	V $-C_2$. At 18° C. (1912).	VI. $-C_2$. At 90° C. (1912).
6500	—	0·86	0·75	—	—	—
6494	0·67	0·86	0·73	3·80	3·75	3·90
6472	—	0·86	0·71	3·74	3·73	—
6403	0·70	0·88	0·74	—	3·75	3·91
6450	—	0·87	0·70	—	3·75	—
6439	0·71	0·88	0·74	3·75	3·77	3·91
6169	—	0·85	0·78	—	3·76	—
6163	0·69	0·85	0·78	3·80	3·77	3·85
6122	—	0·87	0·79	3·78	3·77	3·88
6103	0·67	0·87	0·78	3·79	3·75	3·87
5896	0·65	—	0·80	3·70	—	—
5890	0·67	—	0·78	3·75	—	—
5868	—	—	0·78	—	—	3·95
5858	0·71	0·84	—	3·71	—	3·86
5603	—	—	0·70	—	—	—
5601	—	—	0·69	—	3·78	3·97
5599	—	0·85	—	—	—	—
5595	—	0·85	0·69	—	3·74	3·86
5590	0·69	0·83	0·71	3·77	3·77	3·86
5582	—	—	—	—	3·73	—
5513	0·65	—	0·64	—	—	—
5270	0·63	—	0·72	3·78	3·75	3·89
5265	—	—	0·73	—	3·71	—
5262	—	—	0·70	—	—	—
5189	0·64	—	0·72	3·81	—	—
5042	0·59	—	0·73	3·79	—	—
4878	0·60	0·87	0·77	3·84	3·80	—
4807	—	—	—	—	3·78	—
4586	0·58	0·83	0·76	3·86	3·87	3·96
4582	0·58	—	0·73	—	—	4·00
4527	0·52	0·79	—	3·85	—	—
4456	0·60	0·77	0·71	3·89	3·75	4·01
4436	0·59	0·75	0·73	3·90	3·75	3·98
4426	0·59	0·75	0·76	3·86	3·75	3·98
4319	0·57	0·72	0·60	3·86	3·75	—
4308	—	0·72	0·64	3·86	3·76	3·87
4303	0·60	0·74	0·67	3·87	3·77	—
4299	—	0·72	0·64	3·84	3·78	3·91
4290	—	—	—	3·81	3·77	—
4283	0·58	0·75	0·66	3·84	3·81	—
4227	—	—	—	3·84	—	3·88
3969	0·58	0·75	0·64	—	—	—
3934	0·54	0·72	0·64	—	—	—

The gaps in the above table are due to the fact that many lines gave measurable images on one plate but not on another.


⊙ ····· Observations at 90°C (1912)
× —— „ 18°C (1912)
+ - - - „ 15°C (1909)
Values of $-C_2$
4·0
3·9
3·8
3·7
Values of $-C_1$
·9
·8
·7
·6
·5
·4
4000
4500
5000
5500
6000
6500
Wave-lengths, in Ångstrom units.

The results are exhibited in the diagrams of fig. 2, the base line being shifted so as to bring the curves of C_1 and C_2 close to one another for purposes of comparison.

The curves running through the observations are merely put in as guides to the eye, to call attention to the general trend of the observations. They are not intended in any way to represent accurately the "best fitting" curves.

7. If we compare the 1912 observations at the two temperatures it appears that the coefficient C_2 is numerically increased, C_1 numerically diminished, by rise of temperature.

If, however, we now compare the 1912 observations at the lower temperature with the 1909 observations at a sensibly equal temperature, we get tolerable agreement as regards C_2 but a serious difference in C_1, which cannot be explained away by errors of observation.

The conclusion seems forced upon us that these stress-optical properties are not permanently fixed, but vary with the time and with the life-history of each individual piece of glass.

Possibly a slow readjustment of internal conditions takes place inside the glass, analogous to the settling down of highly viscous material.

But possibly also, the coefficients may be altered by the treatment received by the piece of glass in the interval. Now, of the 1912 measurements, those at the higher temperature were taken on January 18 and February 29, those at the lower temperature on March 7 for C_1 and March 14 for C_2. It is therefore possible that the general shift of the C_1 curve represents the residual effect after heating. No observations were taken in 1912 before applying heat: an omission which unfortunately cannot now be repaired. But clearly the effect of previous treatment will now have to be carefully studied.

One statement, at any rate, we can make with some certainty: the rise of temperature causes a temporary increase of the coefficient C_2.

As regards the general trend of the curves there is in all the C_1 curves a slight average fall from red to blue and in all the C_2 curves a slight average rise from red to blue. This seems unaffected by change of temperature.

Superimposed upon this general trend are local irregularities of the type already discussed in the paper several times referred to. These may or may not be significant. A rise between λ 4300 and λ 4600 occurs in all the curves representing observations taken at temperature 90° C. or after the glasses had been raised to that temperature: there seem to be traces of this rise in the 1909 observations of C_2. Probably this irregularity is significant and is made prominent by rise of temperature. In this connection it may be well to note that the ordinary dispersion of this glass shows anomaly near λ 4300.

One other local irregularity seems worthy of notice; this is the dip in the C_1 curve at 90° C. near λ 5500. This is isolated: there is nothing corresponding to it in any of the other curves. This dip appears, however, well supported by the neighbouring observations. If it prove real it is of considerable interest, being apparently developed only at the higher temperature.

8. In conclusion I have to express my very best thanks to Dr. E. N. da C. Andrade for his invaluable assistance. Dr. Andrade very kindly undertook to measure for me the spectrograms and has expended much valuable time and care upon this task.

My acknowledgments are also due to Professor F. T. Trouton for continuing to me the kind and helpful hospitality of his laboratory at University College, London.

Transparence or Translucence of the Surface Film produced in Polishing Metals.

By G. T. Beilby, F.R.S.

(Received January 21,—Read February 12, 1914.)

[Plate 11.]

In a communication to the British Association[*] it was suggested that all smooth metal surfaces are covered with an enamel-like transparent layer. In a subsequent communication to the Royal Society[†] the actual formation of a surface layer or skin by polishing was demonstrated. Two of the photomicrographs in the latter paper (figs. 5 and 6, Plate 9) showed that minute pits on a polished surface of antimony had been covered over by a film of this description. It was suggested that the diminished reflecting power of the film covering the pits probably indicated that it had become translucent, but no direct evidence of this translucence was afforded by these particular observations. It was also suggested that the film might have been carried across the pits on a support provided by small granules or flakes which had filled up the pit to the level of the general surface. The purpose of the present communication is to record and illustrate certain recent observations which show:—

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[*] 'Brit. Assoc. Rep.,' 1901, p. 604.

[†] 'Proc. Roy. Soc.,' A, vol. 72, p. 218.

(1) That the film which covers the pits is transparent, or at any rate highly translucent; and

(2) That in the case of the smaller pits the mobile film has been carried across the empty pit without any support from below.

In the casting and working of copper, unless certain precautions are taken, the metal is always more or less spongy, owing to the presence of gas bubbles. When the surface of this metal is ground and polished, some of the gas bubbles are laid open and appear on the surface as tiny pits. If the cast metal has been subjected to cold working, by rolling or otherwise, the larger bubbles are distorted, and take elongated and other varied forms. By any method of polishing which will give a fair surface the pits are flowed over and obliterated, but by lightly etching the surface with a solvent the surface skin can be removed and the pits are again disclosed. By careful regulation of the action of the solvent it is possible to remove the surface layer step by step, and the film covering the pits can be reduced to extreme thinness. Through this thin film one seems to be looking right into the pit.

In polishing metal surfaces the amount of the metal which is removed by the polishing agent can be varied through wide limits under conditions which need not be specified here. It is sufficient for the present purpose to state that by suitable methods the skin developed on the surface may be raised to a maximum thickness or reduced to a minimum. For the present inquiry it was desirable that the film produced should be as thin as possible.

The copper used in these experiments received its final polishing on fine linen stretched over a hard flat surface and moistened with one of the ordinary commercial brass polishing liquids. On the copper surface prepared in this way the pits, as seen under high magnification, appear as blue spots on the pale rose-coloured ground of the solid metal. While some of the film-covered pits appear uniformly blue, others show patches of red at various parts of their surface. When these red patches were first noticed it was supposed that they indicated a thickening of the film at these points to the extent necessary for normal reflection. More careful study has shown that the red patches are due to reflections from the inner concave surface of the pit. The beam of light from the vertical illuminator behind the back lens of the object-glass of the microscope passes through the film covering the pit, strikes the concave metallic surface, and is reflected back through the film to the object-glass and thence to the eye-

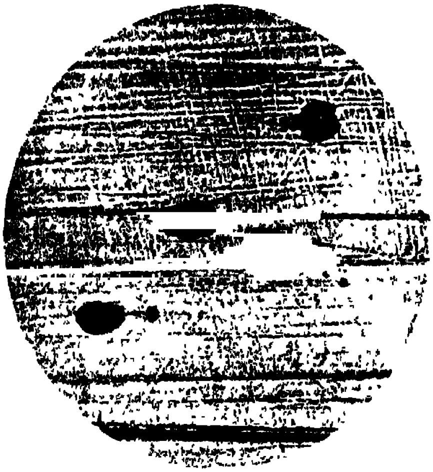

Fig 1 ×800
Film covering Pits

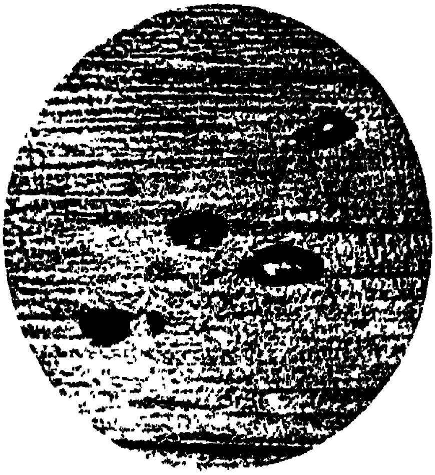

Fig 2
Film removed

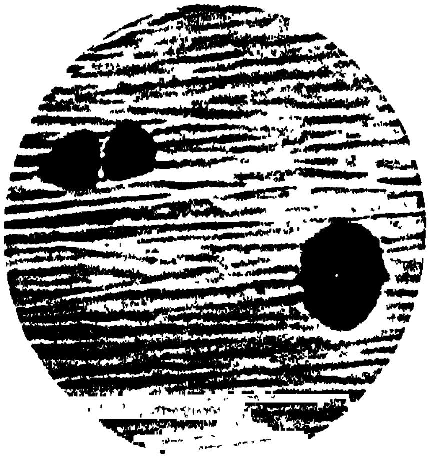

Fig 3 ×1800
Film covering Pits

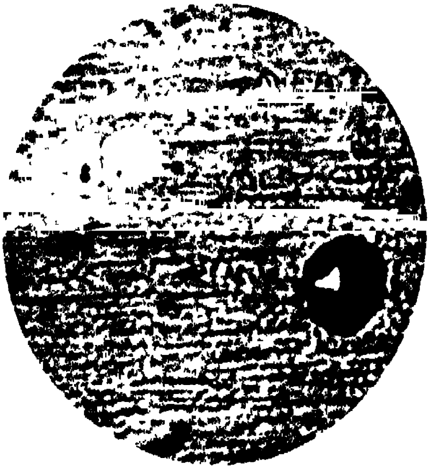

Fig 4
Film removed

piece. The reflecting surface of the pits is evidently far from optical perfection, and the reflected beam is therefore more or less broken up by irregularities of the reflecting surface.

By the use of autochrome plates it has been possible to obtain high power photo-micrographs in natural colours of pits on a copper surface. Four of these transparencies have been reproduced by the three-colour process, and are shown on Plate 11. Figs. 1 and 2 are at a magnification of 800 diameters, and figs. 3 and 4 at 1800 diameters. In figs. 1 and 3 the pits are covered by a blue film, but show patches of red on the blue. Figs. 2 and 4 show the same pits after the film has been dissolved and removed by a 10-per-cent. solution of ammonium persulphate acting for 20 to 30 seconds. On comparing the members of each pair, 1 with 2, and 3 with 4, it is seen that the red patches in 1 and 3 correspond with the spots of light reflected from the concave surfaces of the uncovered pits as shown in 2 and 4.

It is clear that the pits which show these reflections from the under surface must have been practically empty when they were covered by the film, so that the film during its flow was quite unsupported from below.

The thickness of the films covering the pits is probably of the order of 10 to 20 micro-millimetres.

OBITUARY NOTICES

OF

FELLOWS DECEASED.

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SIR GEORGE HOWARD DARWIN, 1845–1912.

BY the death of Sir GEORGE HOWARD DARWIN, which took place on December 7 last, the Society has lost an investigator of rare skill and untiring patience, whose work has done much to add lustre to a name already pre-eminent in the annals of British science.

Sir George, the second son of Charles Darwin, was born at Down, Kent, in the year 1845. Brought up amidst scientific surroundings from the start, he received his early education privately at the hands of Rev. Charles Pritchard, who afterwards became Savilian Professor of Astronomy in the University of Oxford. Among Pritchard's pupils at the time were numbered the sons of many of England's leading scientists, and many of these in turn have since won for themselves distinguished careers, no fewer than three having officiated in after years as Presidents of the British Association.

He gained an entrance scholarship and entered at Trinity College, Cambridge, in 1864, and graduated as Second Wrangler and Smith's Prizeman in the year 1868. The same year he was elected to a Fellowship at Trinity College. The Senior Wrangler of the year was Mr. Fletcher Moulton of St. John's (now Lord Justice of Appeal), who relates how he himself at first remained at Cambridge with the object of pursuing an academic career while Darwin proceeded to London to read with a prominent barrister with a view to adopting the bar as a profession. He was duly called but never practised, and a few years only elapsed before the positions were interchanged and Darwin once more returned to Cambridge, where the rest of his life was spent. There he devoted himself to the solution of those intricate problems, associated primarily with the unravelling of the early history of the Solar System, which form the subject of the four monumental volumes of 'Collected Papers' recently issued under his personal supervision by the Cambridge University Press.

This work had already made considerable progress when he was invited to occupy the Plumian Chair of Astronomy, which became vacant by the death of Challis in 1883, and in the following year he was re-elected to a professorship at Trinity, his previous tenure having expired by lapse of time in 1878. The same year he married Maud, daughter of Charles du Puy, of Philadelphia, and took up his abode at the pleasant home of Newnham Grange at the end of the "Backs," which will long be associated with kindly recollections by all whose privilege it was to visit there. He had two sons and two daughters. His elder son Charles followed in his father's footsteps by becoming a scholar of Trinity in 1905 and graduating as Fourth Wrangler in the Mathematical Tripos of 1909.

Darwin's earliest notable contribution to science was an investigation "On the Influence of Geological Changes on the Earth's Axis of Rotation" ('Phil.

Trans.,' 1877, Part I, vol. 167). At this time the opinion was frequently held by geologists that the wanderings of the pole in the Earth's figure caused by geological upheavals and subsidences, together with associated changes in the obliquity of the ecliptic and the consequent variation in the intensity of seasonal changes, could afford an adequate explanation of the glacial epochs, though the best physical opinion was opposed to this view.

Darwin attacked this problem in characteristic manner. Not content with the mere qualitative indications of analysis his aim was to subject the results which might arise therefrom to definite numerical tests, and though the vagueness of the geological evidence available was such as to preclude any great precision in the results, the conclusions arrived at are quantitatively such as to be "absolutely inconsistent with the sensational speculations as to the causes and effects of the glacial epoch which some geologists have permitted themselves to make."

This paper was referred by the Society to Sir William Thomson (Lord Kelvin), and in this manner was the means of bringing Darwin into association with him. The acquaintance thus formed ripened into a close and intimate friendship which lasted till Kelvin's death. Henceforth we find the well known inspiring influence of Lord Kelvin pervading Darwin's work, and important memoirs followed one another in quick succession.

The conclusions arrived at in the paper referred to above were based on the assumption that throughout geological history, apart from slow geological changes, the Earth would rotate sensibly as if it were rigid. It is shown that a departure from this hypothesis might possibly account for considerable excursions of the axis of rotation within the Earth itself, though these would be improbable, unless, indeed, geologists were prepared to abandon the view "that where the continents now stand they have always stood"; but no such effect is possible with respect to the direction of the Earth's axis in space. Thus the present condition of obliquity of the Earth's equator could in no way be accounted for as a result of geological change, and a further cause had to be sought. Darwin foresaw a possibility of obtaining an explanation in the frictional resistance to which the tidal oscillations of the mobile parts of a planet must be subject. The investigation of this hypothesis gave rise to a remarkable series of papers of far reaching consequence in theories of cosmogony and of the present constitution of the Earth.

In the first of these papers, which is of a preparatory character, "On the Bodily Tides of Viscous and Semi-elastic Spheroids, and on the Ocean Tides on a Yielding Nucleus" ('Phil. Trans.,' 1879, vol. 170), he adapts the analysis of Sir William Thomson, relating to the tidal deformations of an elastic sphere, to the case of a sphere composed of a viscous liquid or, more generally, of a material which partakes of the character either of a solid or a fluid according to the nature of the strain to which it is subjected. For momentary deformations it is assumed to be elastic in character, but the elasticity is considered as breaking down with continuation of the strain in such a manner that under very slow variations of the deforming forces it will behave sensibly as if it were a viscous liquid. The exact law assumed by Darwin was dictated rather by mathematical exigencies than by any experimental justification, but the evidence afforded by the flow of rocks under continuous stress indicates that it represents, at least in a rough manner, the mechanical properties which characterise the solid parts of the Earth.

The chief practical result of this paper is summed up by Darwin himself by saying that it is strongly confirmatory of the view already maintained by Kelvin that the existence of ocean tides, which would otherwise be largely masked by the yielding of the ocean bed to tidal deformation, points to a high effective rigidity of the Earth as a whole. Its value, however, lies further in the mathematical expressions derived for the reduction in amplitude and retardation in phase of the tides resulting from viscosity which form the starting point for the further investigations to which the author proceeded.

The retardation in phase or "lag" of the tide due to viscosity implies that a spheroid as tidally distorted will no longer present a symmetrical aspect as viewed from the disturbing body which generates the tides, as it would do if no such cause were operative. The attractive forces on the nearer and more distant parts will consequently form a non-equilibrating system with resultant couples tending to modify the state of rotation of the spheroid about its centre of gravity. The action of these couples, though exceedingly small, will be cumulative with lapse of time, and it is their cumulative effects over long intervals which form the subject of the next paper, "On the Precession of a Viscous Spheroid and on the Remote History of the Earth" ('Phil. Trans.,' 1879, vol. 170, Part II, pp. 447–530). The case of a single disturbing body (the Moon) is first considered, but it is shown that if there are two such bodies raising tidal disturbances (the Sun and Moon) the conditions will be materially modified from the superposed results of the two disturbances considered separately. Under certain conditions of viscosity and obliquity the obliquity of the ecliptic will increase, and under others it will diminish, but the analysis further yields "some remarkable results as to the dynamical stability or instability of the system . . . . for moderate degrees of viscosity, the position of zero obliquity is unstable, but there is a position of stability at a high obliquity. For large viscosities the position of zero obliquity becomes stable, and (except for a very close approximation to rigidity) there is an unstable position at a larger obliquity, and again a stable one at a still larger one."

The reactions of the tidal disturbing force on the motion of the Moon are next considered, and a relation derived connecting that portion of the apparent secular acceleration of Moon's mean motion, which cannot be otherwise accounted for by theory, with the heights and retardations of the several bodily tides in the Earth. Various hypotheses are discussed, but with the conclusion that insufficient evidence is available to form "any estimate having any pretension to accuracy . . . . as to the present rate of tidal friction."

But though the time scale involved must remain uncertain, the nature of the physical changes that are taking place at the present time is practically free from obscurity. These involve a gradual increase in the length of the day, of the month, and of the obliquity of the ecliptic, with a gradual recession of the Moon from the Earth. The most striking result is that these changes can be traced backwards in time until a state is reached when the Moon's centre would be at a distance of only about 6000 miles from the Earth's surface, while the day and month would be of equal duration, estimated at about 5 hours 36 minutes. The minimum time which can have elapsed since this condition obtained is further estimated at about 54 million years. This leads to the inevitable conclusion that the Moon and Earth at one time formed parts of a common mass and led to an inquiry as to how and why the planet broke up. The most probable hypothesis appeared to be that, in accordance with Laplace's nebular hypothesis, the planet, being partly or wholly fluid, contracted, and thus rotated faster and faster, until the ellipticity became so great that the equilibrium was unstable.

The tentative theory put forward by Darwin, however, differs from the nebular hypothesis of Laplace in the suggestion that instability might set in by the rupture of the body into two parts rather than by the casting off of a ring of matter, somewhat analogous to the ring of Saturn, to be afterwards consolidated into the form of a satellite.

The mathematical investigation of this hypothesis forms a subject to which Darwin frequently reverted later, but for the time he devoted himself to following up more minutely the motions which would ensue after the supposed planet, which originally consisted of the existing Earth and Moon in combination, had become detached into two separate masses. In the final section of a paper "On the Secular Changes in the Elements of the Orbit of a Satellite revolving about a Tidally Distorted Planet" ('Phil. Trans.,' 1880, vol. 171), Darwin summarises the results derived in this and preceding memoirs. Various factors ignored in the earlier investigations, such as the eccentricity and inclination of the lunar orbit, the distribution of heat generated by tidal friction and the effects of inertia, were duly considered and a complete history traced of the evolution resulting from tidal friction of a system originating as two detached masses nearly in contact with one another and rotating nearly as though they were parts of one rigid body. Starting with the numerical data suggested by the Earth-Moon system, "it is only necessary to postulate a sufficient lapse of time, and that there is not enough matter diffused through space to resist materially the motions of the Moon and Earth," when "a system would necessarily be developed which would bear a strong resemblance to our own." "A theory, reposing on *veræ causæ*, which brings into quantitative correlation the lengths of the present day and month, the obliquity of the ecliptic, and the inclination and eccentricity of the lunar orbit, must, I think, have strong claims to acceptance."

Confirmation of the theory is sought and found, in part at least, in the case of other members of the solar system which are found to represent various stages in the process of evolution indicated by the analysis.

The application of the theory of tidal friction to the evolution of the Solar System and of planetary sub-systems other than the Earth-Moon System is, however, reconsidered later, "On the Tidal Friction of a Planet attended by Several Satellites, and on the Evolution of the Solar System" ('Phil. Trans.,' 1882, vol. 172). The conclusions drawn in this paper are that the Earth-Moon system forms a unique example within the Solar System of its particular mode of evolution. While tidal friction may perhaps be invoked to throw light on the distribution of the satellites among the several planets, it is very improbable that it has figured as the dominant cause of change in any of the other planetary systems or in the Solar System itself.

These researches were followed by a further application of Lord Kelvin's analysis of the strain in an elastic sphere to the determination of the strength of the materials of which the Earth must be built so as to prevent the continents from sinking and the sea-bed from rising—"On the Stresses caused in the Interior of the Earth by the Weight of Continents and Mountains" ('Phil. Trans.,' 1882, vol. 173). In this paper it is conclusively shown that the surface inequalities of the Earth's surface must give rise to enormous stress even at considerable depths comparable with the dimensions of the globe itself, and the continued resistance to this stress must imply a strength of material at least equivalent to that of granite. If this resistance is located in the surface layers only a still higher and almost inconceivable degree of strength will be indicated. Thus additional evidence is afforded by the dimensions of superficial inequalities of the Earth's crust of the solid structure of the Earth advocated by Lord Kelvin.

Simultaneously with the above researches we find Darwin, in conjunction with his brother, Mr. Horace Darwin, conducting experiments, in accordance with a suggestion of Lord Kelvin, for the purpose of directly measuring the deflections of the plumb-line due to the disturbing action of the Moon. The experiments failed in their purpose, not from want of delicacy of the apparatus used, but from the existence of more pronounced disturbing influences at the time but little understood, but which nowadays form the subject of continued observation by seismologists. The experiments afford an early contribution to the scientific study of these seismic disturbances; the separation of the lunar disturbances from them has since been successfully accomplished by Hecker.

The application of the theoretical researches on tidal friction to the consideration of the present structure of the Earth demanded observational data to be derived from existing knowledge of ocean tides. As the principal tides might be expected to depart far from the equilibrium law, and an adequate dynamical theory, on account of the complex distribution of the ocean, appeared to be far beyond the possibilities of mathematical analysis, such evidence as was required had to be sought in the separation from the records of tidal observation of the tides of long period which might be expected to follow more closely the equilibrium law. This separation required a close and delicate analysis.

The theory underlying this analysis had been already laid down by Laplace, who had shown how the disturbing force may be analysed into various simple harmonic constituents, each of which will generate a tide of the same period as the disturbing force, the determination of the amplitude and phase of which, though not yielding to theory, can be effected for each port by direct observation.

The practical application of this theory to the discussion of tidal observations by means of harmonic analysis had been suggested by Lord Kelvin, and reports on the subject had been drawn up by him and presented to the British Association in 1868, 1870, 1871, 1872, and 1876. The whole subject was, however, in need of co-ordination and revision, and for this purpose a committee, consisting of Prof. Adams and Darwin, was appointed in 1882. The work of this committee devolved principally on Darwin, who, however, acknowledges the great benefit derived from the advice received from Adams from time to time. The output of this committee consists of a series of reports, dealing in a most thorough and complete manner with the co-ordination of the various existing methods of discussion of tidal observations, the derivation of harmonic constants with the highest degree of precision of which the observations permit, and the utilisation of these constants for the formation of tide tables. The schemes put forward by Darwin in these reports, of which a further account is given at length in the article "Tides," written by him for the 'Encyclopædia Britannica' in 1888, have since been practically universally adopted.

Following on this, we find Darwin turning his attention back to the problems arising in connection with the genesis of the Moon, in accordance with the indications previously arrived at from the theory of tidal friction. It appeared to be of interest to trace back the changes which would result in the figures of the Earth and Moon, owing to their mutual attraction, as they approached one another. The analysis is confined to the consideration of two bodies supposed constituted of homogeneous liquid. At considerable distances the solution of the problem thus presented is that of the equilibrium theory of the tides, but, as the masses are brought nearer and nearer together, the approximations available for the latter problem cease to be sufficient. Here, as elsewhere, when the methods of analysis could no longer yield algebraic results, Darwin boldly proceeds to replace his symbols by numerical quantities, and thereby succeeds in tracing, with considerable approximation, the forms which such figures would assume when the two masses are nearly in contact. He even carries the investigation farther, to a stage when the two masses in part overlap. The forms obtained in this case can only be regarded as satisfying the analytical, and not the true physical conditions of the problem, as, of course, two different portions of matter cannot occupy the same space. They, however, suggest that, by a very slight modification of the conditions, a new form could be found, which would fulfil all the conditions, in which the two detached masses are united into a single mass, whose shape has been variously described as resembling that of an hour-glass, a dumb-bell, or a pear. This confirms the suggestion previously made that the origin of the Moon was to be sought in the rupture of the parent planet into two parts, but the theory was destined to receive a still more striking confirmation from another source.

While Darwin was still at work on the subject, there appeared the great memoir by M. Poincaré, "Sur l'équilibre d'une masse fluide animée d'un mouvement de rotation" ('Acta Math.,' vol. 7).

The figures of equilibrium known as Maclaurin's spheroid and Jacobi's ellipsoid were already familiar to mathematicians, though the conditions of stability, at least of the latter form, were not established. By means of analysis of a masterly character, Poincaré succeeded in enunciating and applying to this problem the principle of exchange of stabilities. This principle may be briefly indicated as follows: Imagine a dynamical system such as a rotating liquid planet to be undergoing evolutionary change such as would result from a gradual condensation of its mass through cooling. Whatever be the varying element to which the evolutionary changes may be referred, it may be possible to define certain relatively simple modes of motion, the features associated with which will, however, undergo continuous evolution. If the existence of such modes has been established, M. Poincaré shows that the investigation of their persistence or "stability" may be made to depend on the evaluation of certain related quantities which he defines as coefficients of stability. The latter quantities will be subject to evolutionary change, and it may happen that in the course of such change one or more of them assumes a zero value. Poincaré shows that such an occurrence indicates that the particular mode of motion under consideration coalesces at this stage with some other mode which likewise has a vanishing coefficient of stability. Either mode will, as a rule, be possible before the change, but whereas one will be stable the other will be unstable. The same will be true after the change, but there will be an interchange of stabilities, whereby that which was previously stable will become unstable, and *vice versâ*. An illustration of this principle was found in the case of the spheroids of Maclaurin and the ellipsoids of Jacobi. The former in the earlier stages of evolution will represent a stable condition, but as the ellipticity of surface increases a stage is reached where it ceases to be stable and becomes unstable. At this stage it is found to coalesce with Jacobi's form which involves in its further development an ellipsoid with three unequal axes. Poincaré shows that the latter form possesses in its earlier stages the requisite elements of stability, but that these in their turn disappear in the later developments. In accordance with the principle of exchange of stabilities laid down by him, the loss of stability will occur at a stage where there is coalescence with another form of figure, to which the stability will be transferred, and this form he shows at its origin resembles the pear which had already been indicated by Darwin's investigation. The supposed pear-shaped figure was thus arrived at by two entirely different methods of research, that of Poincaré tracing the processes of evolution forwards and that of Darwin proceeding backwards in time.

The chain of evidence was all but complete; it remained, however, to consider whether the pear-shaped figure indicated by Poincaré, stable in its earlier forms, could retain its stability throughout the sequence of changes necessary to fill the gap between these forms and the forms found by Darwin.

In later years Darwin devoted much time to the consideration of this problem. Undeterred by the formidable analysis which had to be faced, he proceeded to adapt the intricate theory of Ellipsoidal Harmonics to a form in which it would admit of numerical application, and his paper on "Ellipsoid Harmonic Analysis" ('Phil. Trans.,' A, 1901, vol. 197), apart from the application for which it was designed, in itself forms a valuable contribution to this particular branch of analysis. With the aid of these preliminary investigations he succeeded in tracing with greater accuracy the form of the pear-shaped figure as established by Poincaré, "On the Pear-shaped Figure of Equilibrium of a Rotating Mass of Liquid" ('Phil. Trans.,' A, 1901, vol. 198), and, as he considered, in establishing its stability, at least in its earlier forms. Some doubt, however, is expressed as to the conclusiveness of the argument employed, as simultaneous investigations by M. Liapounoff pointed to an opposite conclusion. Darwin again reverts to this point in a further paper "On the Figure and Stability of a Liquid Satellite" ('Phil. Trans.,' A, 1906, vol. 206), in which is considered the stability of two isolated liquid masses in the stage at which they are in close proximity, *i.e.*, the condition which would obtain, in the Earth-Moon System, shortly after the Moon had been severed from the Earth. The ellipsoidal harmonic analysis previously developed is then applied to the determination of the approximately ellipsoidal forms which had been indicated by Roche. The conclusions arrived at seem to point, though not conclusively, to instability at the stage of incipient rupture, but in contradistinction to this are quoted the results obtained by Jeans, who considered the analogous problems of the equilibrium and rotation of infinite rotating cylinders of liquid. This problem is the two-dimensional analogue of the problems considered by Darwin and Poincaré, but involves far greater simplicity of the conditions. Jeans finds solutions of his problem strictly analogous to the spheroids of Maclaurin, the ellipsoids of Jacobi, and the pear of Poincaré, and is able to follow the development of the latter until the neck joining the two parts has become quite thin. He is able to establish conclusively that the pear is stable in its early stages, while there is no evidence of any break in the stability up to the stage when it divides itself into two parts.

Reference must now be made to Darwin's work on the subject of "Periodic Orbits." Though no published work on this subject appeared before the year 1897, the memoir which then appeared contained the substance of work which had occupied him for some years previously, the continuation of which only ceased with his death. The work had its origin in the beautiful memoirs of Mr. G. W. Hill on the Lunar Theory. The usual method of procedure in discussing "the problem of three bodies" is to base the solution on the "problem of two bodies," *i.e.*, on the theory of elliptic motion, and then to calculate by successive approximations the small disturbances resulting from the presence of a third body. Hill was the first to show that certain special solutions of a simple character could be derived which presented marked superiority over the elliptic orbits previously used as a starting point for more exact investigation. As applied to the Lunar Problem he succeeded in determining by analytical methods a solution in which all those inequalities (the variational inequalities) dependent on the ratios of the mean motions of the Sun and Moon, but independent of the eccentricity and inclination of the lunar orbit and of the Sun's parallax, are taken into account at the outset. Owing to the slow convergence of the series involved, the analytical methods fail when the ratio of the month to the year is increased much beyond the value which actually holds, but Hill showed that in such cases the special solutions could still be derived by a method of numerical quadrature.

The initial object of Darwin's research was to apply Hill's method of investigation to cases which departed somewhat widely from the traditional cases dealt with in the lunar and planetary theories, and where strictly analytical methods were of little avail. He therefore adopts the method of numerical quadratures from the outset. The problem which he set himself was to trace out the possible paths of a small body (or satellite) moving in the plane of the circular orbit of a planet (Jove) round the Sun ; from among such possible paths he then sought to pick out, by trial and error, the particular ones which fulfilled the condition of Hill's lunar orbit, viz., that after the lapse of a certain interval the conditions which obtained at the commencement of the interval would be exactly reproduced, so that the solution obtained would be "periodic" in character. Thus, it would only be necessary to investigate the features pertaining to a single period to obtain a knowledge of the motion of the satellite for all time.

In order to emphasise the phenomena of perturbation, Darwin started with a case where the mass of the planet was considerable compared with that of the Sun. The actual numerical value adopted for the ratio of the masses of the planet and Sun was 1 : 10, and this was adhered to throughout. The differential equations of motion admit of one integral, Jacobi's integral, which introduces an arbitrary constant (C), the constant of relative energy. It was found convenient to classify the orbits in accordance with the value of this constant.

Following Hill, Darwin shows that for large values of C, the orbits described will all be contained either within a closed curve surrounding the planet, within a similar closed curve surrounding the Sun, or outside a closed curve which surrounds both of the former. The three cases correspond with the lunar theory, planetary theory as applied to an inferior planet, and planetary theory as applied to a superior planet.

For smaller values of C, however, the different branches of these limiting curves unite, and passages are opened up through which a satellite may be transferred from one of the spaces to another. The great point of interest was to investigate the features associated with such a transference, and consequently the investigation was limited to the smaller values of C which would permit of this possibility. Even with the further limitation that "simply" periodic orbits alone (*i.e.*, those which repeat themselves after a single revolution round the Sun, or primary) were considered, the amount of work required was found to be prodigious. The interest in the subject was sustained by the continued surprises which the results yielded, and he was thus induced to continue computing more and yet more orbits whose forms appeared to be typical. Many of these were of a highly complex character, the arithmetical determination in such cases being almost always highly evasive.

Not content with merely indicating the forms of these orbits, he set himself in every case the still more difficult task of discussing their stability. In order that a satellite may describe a periodic orbit it must satisfy ideal initial conditions, any departure from which will cause it to describe initially a closely adjacent orbit. For certain orbits the disturbed orbit will oscillate in relation to the periodic orbit in a period which is associated only with the properties of the latter orbit, and is independent of the nature of the disturbance, provided only the latter be small. This was the case with Hill's variational orbit, but in other instances an alternative presents itself in which the quantity, which figures analytically as the period of the disturbance, presents itself as an imaginary or complex quantity. In such a case the amplitude of the oscillations will increase with greater or less rapidity, and the disturbed orbit will soon cease to follow even approximately the course of the periodic orbit. In the latter case the periodic orbit is said to be unstable.

The problem of determining the periods of the small oscillatory disturbances, whether of real or imaginary period, is identical with that dealt with by Hill in his determination of the motion of the lunar perigee. Darwin at first followed Hill's methods, in which the solution is derived by the reduction of a determinant of infinite order, but later an alternative method depending on quadratures was devised. But whichever plan was used the computations were found to be exceedingly laborious, and for orbits with sharp flexures almost intractable. Nevertheless, in almost every case he is able to arrive at a definite conclusion as to the stability or otherwise of the orbits traced.

The subject of these investigations was dealt with simultaneously by Poincaré in his volumes dealing with "Les Nouvelles Méthodes de la Mécanique Céleste." Both authors derived their inspiration from Hill's work, but the methods of treatment differ as widely as do their respective methods of treatment of the problem of the figures of equilibrium of rotating fluid. Poincaré's method consists in a discussion of the analytical properties of the fundamental differential equations of dynamics, and from his vast knowledge of the theory pertaining to such equations to deduce properties of their solutions without actually deriving the solutions. However much one may admire Poincaré's skill and insight in dealing with abstruse mathematical analysis, to many readers the abstract process of reasoning will be found unsatisfying, and more concrete presentations of the problems will appear to possess greater lucidity. To all the actual derivation of definite solutions of the problem of three bodies by a process which admits of wide extension will appear as a high achievement. Many will share Darwin's own distrust, based on experience, of the possibility of correctly reasoning without fear of ambiguity about solutions which have not been definitely found, but his own results cannot fail to carry conviction. Darwin's orbits give clear and tangible illustrations of many of the features derived by Poincaré through the medium of his analysis, but from the nature of his methods, which consist in the study of special cases, they do not permit of such wide generalisation. Thus the work of either investigator in a field which, previously to the publication of Hill's great memoir, had come to be considered as practically inaccessible, must be regarded as complementary to that of the other.

We have confined ourselves hitherto to a summary of the more important researches which occupied Darwin's attention. The subjects of these researches were frequently dealt with in his professorial lectures, which, whether he was expounding his own work or that of others, were always marked by singular lucidity. The current topics of investigation were almost always introduced in these lectures and discussed with his students. He was conscientious to a degree in acknowledging any assistance he himself derived in this manner and whether in the lecture room or in his private study was eager to discuss projects for research on collateral subjects. His own enthusiasm communicated itself to his pupils and his influence did much to maintain the traditional reputation of Cambridge as a school of applied mathematics, and this in spite of the fact that, with the growing need for increased specialisation, a strong tendency existed for the separation of the subjects of study into two distinct schools, that of pure mathematics and that of experimental physics.

In University administration he took but little part in internal politics, but in matters concerning the relationship of the University with external bodies his influence was great and his services were always available. In the formation of the Cambridge University Association for the purpose of raising increased funds for University purposes he took a leading part, as also in the scheme for an Employment Bureau to bring University candidates more prominently into touch with the various openings that presented themselves in after walks of life on completion of their University course.

Outside the University his services were in demand in connection with the various learned societies with which he was associated.

For the Royal Society he frequently served on Committees and officiated as a referee for numerous papers. He was President of the Royal Astronomical Society in the year 1889–1900, when it devolved on him to deliver an appreciative address on delivering the Gold Medal of the Society to his famous co-worker Poincaré. This address has been referred to by those who were privileged to hear it as one of the most inspiring that has ever been heard from that Chair on a similar occasion.

An event of great importance in his life was the occasion on which he was invited to occupy the Presidential Chair of the British Association in 1905, on the occasion of its visit to South Africa. The task was an exceptionally difficult one, involving, besides the delivery of two formal addresses at the two more important centres visited, innumerable minor speeches at almost every place of call *en route;* in each one of which he was exceedingly happy in adapting himself to the occasion. He took no small share in the preliminary organisation for the journey of the Society, and it was largely due to his personality and tact in adjusting minor differences that the arrangements proved so efficient and frictionless in actual operation. His Presidential Address on this occasion deals with a remarkable analogy between the subjects of his own investigations and collateral investigations in biological and political science. On his return to England he received the well-deserved honour of a K.C.B. at the hands of His Majesty.

In 1897 he was invited to America to deliver a course of lectures at Boston and chose as his subject "The Tides." These lectures formed the nucleus of a volume published by him in 1898 under the title of 'The Tides and Kindred Phenomena of the Solar System,' in which a semi-popular account is given of many of his important researches. The book met with a hearty reception and has since passed through many editions and been translated into many foreign languages.

He was nominated as a member of the Meteorological Council soon after his return to Cambridge, and continued to serve as a representative of the Royal Society on the Treasury Committee which superseded that Council a few years ago.

He was appointed by the Foreign Office as the first British representative on the International Geodetic Association, a position which involved him in extensive correspondence with the various geodetic organisations throughout the British Dominions. The choice is admitted by all to have proved an exceedingly happy one, and his services were duly acknowledged by the Association itself when they accepted the invitation, conveyed by him, to hold their triennial meeting in England in 1909, and nominated him as President for the occasion.

He took a leading part in the organisation of the meeting of the fifth International Congress of Mathematicians, which was held at Cambridge on August 22–28 of last year, and, in spite of failing health at the time, fulfilled the duties of the presidency with notable success. The symptoms were, unfortunately, to prove fatal, and, after a protracted illness, he passed peacefully away on December 7 last, to the great sorrow of all who were privileged to know him.

He was a corresponding member of many learned Societies, both in Europe and America, and many honours were conferred on him, in appreciation of his scientific work. The Gold Medal of the Royal Astronomical Society was awarded to him in 1892, and a Royal Medal on the nomination of the Royal Society in 1884, while, shortly before his death, he had the gratification of receiving the greatest mark of distinction which the Society can confer, by the award of the Copley Medal in the year 1911, and in 1912 the Victoria Medal of the Royal Geographical Society.

In private life his characteristic energy showed itself in a multitude of ways, such as in the mass of miscellaneous knowledge he had acquired from books, and in his facility in languages. As a trifling instance may be mentioned his acquaintance with heraldry, in which he had grounded himself as a little boy at Down, daily poring over the abstruse works of Guillim and Edmondson. The careful drawings made from these books doubtless trained his powers of draughtsmanship, which in later life were shown in his illustrations of some of his father's works.*

The same trait might be illustrated in many ways, *e.g.* in the zeal with which as a boy he collected lepidoptera, or the vigour with which as a young man he mastered the difficult game of tennis, just failing, however, to represent his University against Oxford; or again, near the end of his life, in his patient attempt to become an archer. The holidays of life, and especially the pleasures and amusements of his wife and children, were shared by him, and organised with a happy and rapid effectiveness.

Here, and indeed in every relation of life, his energy was coloured and made lovable by that simple sweet open nature which endeared him to so many.

S. S. H.

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* He is mentioned in the 'Fertilisation of Orchids' as having solved the problem of the Musk Orchis (*Herminium monorchis*).

SIR WILLIAM WHITE, 1845-1913.

SIR WILLIAM WHITE died unexpectedly on February 27 last, while engaged in London on his ordinary everyday work, aged 68 years. The world is a loser by his death. He was an ardent worker in many fields, in all of which he gained distinction.

He was born at Devonport in 1845, his father being a native of that town and his mother a native of Lostwithiel. He was the youngest child of a large family, and was given no special educational facilities. Writing of this time afterwards he says: "I had to travel a hard road."

After studying in a small private school in Devonport, where he made the best use of such opportunities as the place afforded, he left it as head boy to become a shipwright apprentice in Devonport Dockyard.

The Admiralty—as Sir William White recalled in his Chairman's Address to the Royal Society of Arts—led the way in the provision of technical education for the youth of this country; and it was in Devonport Dockyard School for Apprentices that Sir William may be said to have commenced that study of Naval Architecture which was to carry him so far.

Side by side with his purely school work, he was engaged at this period in the actual building and repairing of ships, and so acquired that combined scholastic and workshop knowledge of which he was so strong an advocate in later years. This is now generally known as the "sandwich system" of technical training.

In 1864, the Admiralty found themselves faced by a great emergency. The end of the wooden ship-of-war had come, and for the reconstruction of the Navy they needed a steady supply of officers thoroughly trained in the science of Naval Architecture. Under the advice of Mr. E. J. Reed (afterwards Sir E. J. Reed, K.C.B., F.R.S.) and the Council of the Institution of Naval Architects they reverted to a scheme which twice in the century they had abandoned, and they instituted at South Kensington Museum the Royal School of Naval Architecture and Marine Engineering. Sir William White was one of eight shipwright apprentices chosen for its first students. The Admiralty spared no expense to make the training thoroughly efficient, and obtained the services of eminent professors in all branches of science necessary for Naval Architects and Marine Engineers. Sir William was an eager student at this school, and obtained its highest diploma. When he left the school in 1867 he was appointed, with five other pupils, by Sir Edward Reed (the Chief Constructor of the Navy) to the Admiralty Staff for the design and building of H.M. ships. He assisted Sir Edward Reed personally in the preparation of his great work on 'Shipbuilding in Iron and Steel,' published in 1869, and in the preparation of the Memoir on the Stresses on Ships contributed by Sir Edward to the 'Philosophical Transactions' for 1871.

The problems of naval design at this period were numerous, and the most diverse views were held by those in authority. The main questions involved, so far as the ships of the line were concerned, were:—

1. What was the best method of constructing the armoured side of a ship so as to secure the greatest resistance to gunfire?
2. What was the best method of disposing the area of the armour on a ship's side so as to secure a just balance between the protection, in action, of vital fighting parts, and the exclusion of water from other parts of the vessel, where its entry in excessive quantities might lead to the foundering of the ship?
3. What was the best disposition of the armament?
4. Whether, on the whole, it was best to build a short vessel like Sir Edward Reed's *Bellerophon* or a long vessel like the first armoured *Warrior*?

Sir William took up the discussion of these points with such ability as to throw much light on the problems at issue. He also assisted Sir Edward Reed in preparing his book 'Our Ironclad Ships,' which dealt *in extenso* with the question of short *v.* long ship.

In 1870, Sir Edward Reed retired from the position of Chief Constructor of the Navy. The office was then put into Commission, with Sir Nathaniel Barnaby, K.C.B. (then Mr. Barnaby), as Chairman of the Council of Naval Construction, and so well was Sir William's work appreciated by the new head, that he made him Secretary of the Council.

In January, 1871, Lord Dufferin's Committee was appointed "To examine the Designs upon which Ships-of-War have recently been constructed," with special reference to the loss of the *Captain*, and a large calculating staff, composed wholly of men trained at the Royal School of Naval Architecture and Marine Engineering, was formed at the Admiralty under Mr. F. K. Barnes, Member of the Council of Construction, for the purpose of preparing data for the Committee. Numerous calculations concerning the stability, strength, and other features of existing ships were demanded, and these had to be much more thorough in character than was at that time customary. In this work Sir William took a prominent part.

During this early period of his career Sir William had already shown that devotion to the literature of his profession which was a prominent feature of his career. The first volume of the Annual of the Royal School of Naval Architecture and Marine Engineering was published in 1871 under the direction of a Committee of which Sir William was a member, and although there is no signed paper of his in the volume, he was a large contributor to its contents. In 1871, he, in conjunction with Mr. W. John, submitted a paper to the Institution of Naval Architects on "The Calculation of the Stability of Ships, and some matters of interest connected therewith." This was the first of many papers which he contributed to the Institution of Naval Architects. They were always of first-rate importance. Many of them dealt with matters of Naval policy as distinct from Naval Architecture, and the views which he put forward were always received with great respect. Throughout his whole life he took a vigorous part in the discussion of papers at the Institution, and so late as last year he made a valuable contribution to the discussion of geared turbines and oil engines.

From the beginning of his services at the Admiralty, Sir William much interested himself in the education of young naval architects, and in 1869 he was appointed to succeed his former teacher Mr. Crossland, Member of the Council of Construction, and a distinguished member of an earlier school of Naval Architecture, as Lecturer on Naval Design at the South Kensington School. This position he retained for some years after the transfer in 1873 of the School to the Royal Naval College, Greenwich.

While holding his position, he assisted Dr. T. Archer Hirst, F.R.S., the Director of Studies of Greenwich, in arranging a course of instruction in Naval Architecture for the benefit of executive Naval officers. The syllabus of instruction was so well chosen and so wisely carried out, largely under his guidance, that large numbers of officers were attracted to the classes, which continue in effective operation to the present time.

About this time he also put forward a well considered scheme for the formation of a Royal Corps of Naval Constructors, which was to replace the heterogeneous system then in force. This was adopted by Sir Nathaniel Barnaby and by Sir W. Houston Stewart, K.C.B., the then Controller of the Navy. After consideration on their part, a Committee was appointed, with Sir T. Brassey, now Earl Brassey, as President, to consider this scheme, and in 1883 the Crown, by Order in Council, created the Corps on its existing footing.

Sir William was promoted to the rank of Constructor in 1875, and to that of Chief Constructor in 1881.

The chief designing work on which he was engaged under Sir Nathaniel Barnaby in 1876–77 was that of the famous *Inflexible*, which had two turrets *en échelon*, each containing two 16-inch muzzle-loading guns. The turrets themselves were enclosed in a comparatively short armoured central citadel, and the ends of the ship were unprotected by vertical armour, having armoured decks only.

The design of this vessel excited very strong adverse criticism, led by Sir Edward Reed. A specially competent Committee, consisting of Admiral Sir James Hope, G.C.B., Dr. J. Woolley, Mr. G. W. Rendel, and Mr. W. Froude, F.R.S., was appointed to report on the stability of the vessel, and after long and exhaustive investigation, made both at sea on actual ships, and with models in the experimental tank of Mr. William Froude, the Committee reported that the design fully satisfied the desired conditions. This design was repeated on a smaller scale in the *Ajax* and *Agamemnon*, and in the two somewhat larger vessels *Colossus* and *Edinburgh*, although even these were still much smaller than the *Inflexible*.

Other vessels on which Sir William was engaged during this period, under Sir Nathaniel Barnaby, were the cruiser *Iris* (the first steel vessel built for the Royal Navy), the *Mersey* class of cruiser, and the *Admiral* class of battleship. The *Admiral* class excited fierce criticism on account of their so-called "soft ends," and this criticism did not cease till some time after Sir William's return to the Admiralty in 1885.

From 1883 to 1885, Sir William was engaged as Warship Designer and Manager of the War-Shipbuilding Branch of Messrs. Sir W. G. Armstrong, Whitworth and Co., at Elswick-on-Tyne. He there laid out the new shipyard at Elswick and designed and laid down several vessels for Foreign Powers.

In 1885 he was offered by Lord George Hamilton, then First Lord of the Admiralty, the position of Assistant Controller of the Navy and Director of Naval Construction in succession to Sir N. Barnaby, who had retired on account of ill health, and he accepted the offer and returned to the Admiralty.

At this time some of the vessels of the *Admiral* class were still in course of construction. There were also building the *Victoria* and *Sanspareil* (the former at Elswick Shipyard under his directions), the *Trafalgar, Nile*, and *Hero* battleships; the *Impérieuse* and *Warspite*, and the seven vessels of the *Orlando* battle-cruiser class; the *Rattlesnake*, the first of our so-called torpedo gunboats and the forerunner of our torpedo boat destroyers, was under construction.

Sir William at once proceeded to take up the work of developing naval design, so as to employ to the greatest advantage the material available for attack and for defence.

As regards the cruiser class of vessel, he adhered for some time to the system, first introduced in the Elswick-built Chilian cruiser *Esmeralda* (designed by Mr. George Rendel), of a strong arched steel deck, rising, at the middle line of the ship, somewhat above the water line, and pitched at some feet below the water line where it reached the side of the ship. This system of protection, in conjunction with large coal bunkers flanked on the inside with cofferdams, gave on the whole, he considered, the best protection available under cruiser conditions as then laid down. In this view the Board of Admiralty fully concurred, although the absence of side armour did not escape criticism.

This type of vessel reached its culmination as regards size in the *Powerful* and *Terrible*, and, although side armour had been adopted by other countries for such vessels, it was not till substantial improvements had been made in the quality of armour, that Sir William recommended the Board (in June, 1897) to adopt side armour protection for our cruisers. This led to the laying down of six vessels of the *Cressy* class, followed by four vessels of the *Drake* class, and 10 somewhat smaller vessels of the *Monmouth* class.

As regards smaller cruisers, Sir William designed and built the Australian cruisers of the *Wallaroo* class, and the *Medea, Barrosa*, and *Barham* classes for the Royal Navy.

He made improvements in the design of the torpedo gunboat *Rattlesnake* and produced the *Sharpshooter* and later vessels, which were of a much more habitable type than had previously prevailed.

Sir William's first battleships were the eight vessels of the *Royal Sovereign* class, a development of the *Trafalgar* class in which modifications of the dimensions and the disposition of armament were introduced. The *Royal Sovereign*, the first vessel of the class, was built in less than three years and was completed in 1892.

After close comparative study of the arrangements of armament and protection found in foreign warships then building, and of the rapidly changing engineering factors of the date, he was in a position to make a special analysis of the real elements of fighting efficiency. In 1889, with the sanction of the Admiralty, he read a paper before the Institution of Naval Architects giving his views on the general constructive position, and setting forth the considerations which had influenced the Board in ordering the *Royal Sovereign* class. He was much criticised by some members of the Institution, but it was recognised that he made good the position he had taken up.

The main features of the *Royal Sovereign* class were followed in our own and some foreign navies up to the appearance of the *Dreadnought* in 1905.

During Sir William's tenure of the post of Director of Naval Construction, it was considered necessary by the then Board of Admiralty, owing to the political circumstances of the time (1889), for the Admiralty to make special building efforts. Under a loan embodied in the Naval Defence Act, 70 vessels of various classes were built, and Sir William White carried out his share of this work with complete success.

Sir William served under several successive Boards of Admiralty and received the fullest confidence of all.

Physically strong as he originally was, the work he had done from his appointment as Director of Naval Construction in 1885 gradually undermined his health; and in order to avoid a complete and possibly irremediable breakdown he felt compelled to retire in 1901.

When we consider his long period of service as Chief Constructor of the Navy, the special circumstances which necessitated changes in all types of ships, and the great pressure caused by the construction of the 70 special naval defence ships, his tenure of office must be regarded as highly distinguished. It is a record of which any man might be proud, and for which his country must be grateful.

He was an Honorary Vice-President of the Institution of Naval Architects, Past President of the Institution of Civil Engineers, Chairman of the Royal Society of Arts, and President of many other scientific societies; he was LL.D. of Glasgow, D.Sc. of Cambridge, Durham, and Columbia, was a member of many foreign societies, and held many other similar degrees and honours. He was a Past Master of the Worshipful Company of Shipwrights, and in his association with this Company he did much to promote the professional education of naval architects and marine engineers.

As a Fellow of the Royal Society he did much useful work in connection with the National Physical Laboratory, of the Governing Body and Executive Committee of which he was a member. One of his latest acts in connection with the Laboratory was the securing of a large donation from the Drapers' Company on its behalf.

Sir William had very close connection with various City companies, so far as they assisted in education or the endowment of research, and freely gave his time to assist them in all such matters.

He was a most competent chairman of a meeting on any professional subject, and a ready speaker in general who had always something interesting and useful to say. He was especially expert in carrying a meeting past matters on which there was much discussion, into regions where unanimity prevailed and effective action could be taken. He was a splendid debater, and throughout the long controversy between Sir Edward Reed and the Admiralty as to its shipbuilding policy (especially in regard to the *Inflexible* type and the *Admiral* class of ship), his defence was recognised as brilliant and convincing and after the discussion on the *Royal Sovereign* class already referred to, all serious attacks upon the shipbuilding policy of the Admiralty disappeared, and the utmost confidence prevailed.

These notes have necessarily been confined to a consideration of Sir William White's career as a naval architect, but he was a man of far too wide an outlook to be contained by any limits of profession. After his integrity, ability, and perseverance, the quality which carried him farthest was perhaps the gift of speaking. Speaking was a pleasure to him. He was very fluent, but his words were always well chosen. He was equally good in setting out a proposition, in quick debate and repartee; and in an amusing after dinner speech. He had a great power of marshalling arguments, and of converting opponents by tactical insistence. He wrote much and his writing was unaffected, lucid, and convincing.

He was a man of high ideals and gave his services unsparingly to any deserving cause. He was a thoroughly religious man without being in any way a religionist. Wherever he went he carried with him a wholesome atmosphere. He was a kind and most helpful friend to numbers of young men.

Within a week of his death he wrote to a friend whom he had known for 30 years: "I fear that your recognition of those days puts too high a value upon any help that I then rendered you. But I do claim to have endeavoured all along, and still endeavour, to assist and encourage young men who are making similar efforts, and I have rejoiced greatly in your personal success."

In the annals of the British Navy, Sir William White's name will long be remembered with honour. His career will serve as an example to the Constructive Corps which he did much to originate and to train; and that Corps must always be a potent factor in the maintenance of the naval power of this country. And so we leave him, with a feeling of regret and gratitude for a kindly as well as clever man.

P. W.

with the Laboratory was the securing of a large donation from the Drapers' Company on its behalf.

Sir William had very close connection with various City companies, so far as they assisted in education or the endowment of research, and freely gave his time to assist them in all such matters.

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P. W.

SAMUEL ROBERTS, 1827–1913.

Samuel Roberts was the second son of the Rev. Griffith Roberts, Presbyterian minister, and of Anna, the eldest daughter of Samuel Churchill, a merchant of Exeter. He was born at Hackney, December 15, 1827.

He was educated at Queen Elizabeth's Grammar School, Horncastle, Lincs., his father being minister of the Presbyterian Chapel at Kirkstead, near Horncastle, and resident at Horncastle. He passed from the Grammar School to Manchester New College in June, 1844. He matriculated at the University of London in 1845 with Honours in Classics and Mathematics. He took the B.A. in 1847 with Honours in Mathematics, and the M.A. in 1849, when he was first in Mathematics and Natural Philosophy and obtained the Gold Medal.

He was admitted a solicitor in 1853, having served his articles of clerkship with Mr. Richard Mason, Town Clerk of Lincoln. After some years he gave up practice, removed to London and devoted himself to mathematical research.

He was elected a member of the London Mathematical Society in June, 1865, a few months after its foundation. He was Honorary Treasurer of that Society from 1878–1880, President, 1880–1882. He was elected a Fellow of the Royal Society in 1878, served on the Council of the London Mathematical Society for many years and was the de Morgan Medallist of 1896.

He was twice married; in 1858 to Mary Ann Astley, only child of the Rev. Richard Astley, formerly of Shrewsbury. She died in 1894. In 1896 he married Lucy Elizabeth Holland, second daughter of Philip Henry Holland, surgeon and Government Inspector, who survives him.

By his first marriage he had three sons. The eldest was Samuel Oliver Roberts, M.A., formerly scholar of St. John's College, Cambridge, 7th wrangler in 1882 and later Mathematical Master at Merchant Taylors' School. He died in 1899. The second son is Harry Astley Roberts, B.A. (Lond.), solicitor, who is still living. The third son died in infancy.

He died September 18, 1913, at the ripe age of 86, and was buried in Highgate Cemetery.

The Royal Society Catalogue of Scientific Papers shows that up to the year 1883 he contributed 62 papers to Mathematical Journals. These commenced in 1848 and for about ten years his preference led him to work at geometry and the Calculus of Operations. His most important paper at this time was "On the Transformation of Co-ordinates," published in the 'Quarterly Mathematical Journal' of 1858. The foundation of the London Mathematical Society in 1865 stimulated him to increased activity, and from that date to 1873 a long series of papers were given to the Society's Proceedings and to other journals. These are mostly concerned with geometry and include important contributions, of which may be noted "On the Ovals of Descartes," L.M.S., 1870, "On the Order and Singularities of the Parallel of an Algebraic Curve," L.M.S., 1871, "On the Motion of a Plane under certain Conditions," L.M.S., 1871, "On the Parallel Surfaces of Conicoids and Conics," L.M.S., 1872, "On Professor Cremona's Transformation between two Planes," L.M.S., 1872, "On Parallel Surfaces," L.M.S., 1873.

From the year 1875 he became interested also in the Theory of Numbers, and made some noteworthy contributions to the forms of numbers determined by continued fractions and to Euler's theorem on the product of two sums of four squares. His valedictory address to the London Mathematical Society upon vacating the chair was a masterly discourse entitled "Remarks on Mathematical Terminology and the Philosophic Bearing of recent Mathematical Speculations concerning the Realities of Space," 'L.M.S. Proc.', vol. 14, He has left a considerable mathematical correspondence with de Morgan, Salmon, Cayley, Sylvester and others, and was in intimate friendship with many mathematicians of his day such as Hirst, J. J. Walker, R. Harley, Spottiswoode and Perigal. He had many interests besides mathematics. From his earliest years he worked with the lathe and liked to construct electrical machines and other scientific apparatus. He was devoted to chess, angling and philosophy. He was interested in geology and microscopy and spent much of his leisure in collecting geological specimens for the microscope. He was for many years a member of the Quekett Microscopical Society. For the last ten years of his life he was almost totally blind. This infliction he bore with great patience. Throughout his life he was of a retiring disposition and regarded original research as being its own reward.

As an ardent worker, who made not a few important additions to mathematical science, he will not be soon forgotten.

P. A. M.

JOHN MILNE, 1850–1913.

John Milne, geologist, mining engineer, seismologist, and traveller; Honorary Fellow of King's College, London; F.G.S., D.Sc. (Oxon); Royal Medallist, 1908; Lyell Medallist of the Geological Society, 1894; was born at Liverpool December 30, 1850. He was the only child of John Milne, of Milnrow, Rochdale, and Emma, daughter of James Twycross, J.P., of Wokingham. He married Tone, daughter of Horikawa Noritsune, the high priest of Hakodate. After school at Rochdale and Liverpool he went to King's College, London. Gaining a scholarship he now attended the Royal School of Mines and studied Geology and Mineralogy under Prof. Sir Warrington Smyth. After some practical mining experience in Cornwall and Lancashire he studied Mineralogy at Freiberg and visited the principal mining districts of Germany. At the request of Mr. Cyrus Field he spent two years in investigating the mineral resources of Newfoundland and Labrador (see 'Jour. Geol. Soc.,' 1874; 'Geol. Mag.,' 1876 and 1877). He visited Funk Island, once the home of the Great Auk, and made a large collection of skeletons of that extinct non-flying bird which used to frequent the northern parts of Great Britain. He showed his fondness for travel very early, for at school, when he obtained a money prize just before the holidays, he started for Iceland without parental leave and made his first experience in a very dangerous exploration of the Vatna Jokul. At the much later date of 1874 he joined the expedition of Dr. Beke, which, under the auspices of the Royal Geographical Society, started to investigate what Dr. Beke thought to be the true site of Mount Sinai, in Arabia, east of the Gulf of Akaba (see 'Jour. Geol. Soc.,' 1875). Prof. Milne often spoke of the shallowness of the south end of the Gulf and of the possibility of its being crossed on foot if a strong north-east wind was blowing. About this time he published interesting geological notes on the environs of Cairo ('Geol. Mag.,' 1874).

In 1875 he was appointed Professor of Geology and Mining in the Imperial College of the Public Works Department, Tokio, Japan, and he spent eleven months in reaching Japan. He travelled through Siberia by tarantass and sledge to Kiachta, very much on the line now followed by the railway. He crossed Mongolia with a camel train in the depth of winter, the temperature being usually well below zero Fahrenheit ('Trans. Asiatic Soc. Japan'). His boyhood experience on the Vatna Jokul made this appear commonplace. He passed the Great Wall on January 11, 1876, and travelling through Pekin and Tientsin he reached Shanghai on February 24. In Japan he proved to be an excellent teacher. He made many tedious expeditions through Japan and Yeso studying their geology, but he soon studied little else than earthquakes. At that time, although much had been written about seismology, it was not a science; there were no instruments which truly recorded the motion of the ground. In the course of time, by persistent experimenting, by taking everybody into his confidence and asking for help from all sorts of scientific experts, he invented good instruments and gained a wonderful knowledge of what we now call the science of seismology.

After the destructive earthquake of 1880 he arranged a public meeting which was well attended by Japanese and foreigners; the Seismological Society of Japan was formed at that meeting, with Prof. Milne as Secretary. For fifteen years he directed its work, the results of which are given in twenty volumes of reports, well known to seismologists. The Japanese Government established an Earthquake Committee, which it still supports with an annual subsidy, whose average amount is 10,000 dollars, but which is sometimes as great as 25,000. When he gave up his Professorship in Japan in 1895 he left behind him a well trained staff of seismologists and many observing stations. There are nearly 1000 observing stations now in the Japanese Empire. The Emperor conferred upon him a pension and the Order of the Rising Sun. As to the necessity of numerous observing stations, in 1883 his book on 'Earthquakes' states:—"It is not unlikely that every large earthquake might, with proper instrumental appliances, be recorded at any point on the land surface of our globe." It was some time before this surmise was proved to be true, but it is the foundation of all modern progress in seismology.

Soon after his return to England he settled at Shide, near Newport, in the Isle of Wight. Since that time, as secretary of a committee of the British Association, he has established about 60 observing stations, in selected positions, all over the world. Whatever other instruments there may be in those stations, each of them has one or more specimens of Milne's standard seismometers. Instructions and reports are sent out regularly from Shide to these stations; photographic records are regularly sent to Shide. These are all carefully compared with one another, and an elaborate annual report of the world's seismology is published by the British Association, whose grants to this committee since 1895 have often been as much as £130 per annum. From the Government Grant to the Royal Society it has received altogether £600. Mr. Matthew Gray, one of Milne's personal friends, gave, some years ago, a sum of £1000, which is invested. Prof. Milne's private expenditure on the work of the committee has always been considerable. He has left a bequest of £1000, to help in continuing the work, but this will not take effect till the death of Mrs. Milne. Prof. Judd was for many years the chairman of the committee; he retired in 1907, and Prof. Turner, of Oxford, became chairman. It is hoped that a fund may be formed to enable the work to be continued.

There is not only an observing station at Shide, remote from the dwelling-house, but also, attached to the house, a laboratory, which contains a library and a collection of records, and it is the business centre of administration. An account of the work done at Shide, written in 1912 by Mrs. Lou Henry Hoover, will be found in the 'Bulletin of the Seismological Society of America,' vol. 2, No. 1. Many such accounts have been published, for Shide had always a great number of visitors, of all ranks and from all parts of the world, and Prof. Milne was very hospitable; but Mrs. Hoover gives the best account of how it was that everybody enjoyed and envied his enthusiasm in his work, and admired his unstinted praise for other workers, and the intense youthfulness of a man who was 62 years of age.

His numerous scientific papers show that he followed many side-tracks by persistent strenuous experiment and observation. One that he thought of great importance was the varying photographic effect obtainable from rock surfaces in caves that were light-proof. He saw some connection between this and the great health differences that exist between two neighbouring places. The movement of the ground due to change of tide, the approach of hills due to rainfall, the velocity of waves of the ocean produced by earthquakes, the fracture of submarine telegraph cables, the yielding of rock near places where there are sudden great differences in level, and many other problems, occupied his attention. He was never tired of trying the new instruments invented by himself and others. He instituted methods of building railway bridges and houses in countries subject to earthquakes. He induced railway companies to test the soundness of their tracks and bridges by instruments carried on the trains. The Colonial Office made use of his services, for when all the cables giving telegraphic communication with a colony were simultaneously broken, it was important to know whether the fracture was due to an earthquake or to the machinations of a foreign power. Insurance offices made use of his Shide records, for insurance against earthquake effects has now become a large business. People interested in rebuilding cities, like San Francisco, asked his advice about new structures. Help of these and many other kinds was freely given, even when it involved the expenditure of much time and labour.

A list of his publications is given in an article by his lifelong friend, Dr. Woodward, in the 'Geological Magazine' of August, 1912. From 1874 to 1878, there are papers about Newfoundland, Cairo, the Sinaitic Peninsula, ice, icebergs, and volcanoes. In 1879, there are accounts of his journey to China and his cruise among the Kurile Islands; papers on volcanoes and on the Stone Age in Japan. In that year he published a small treatise on Crystallography. In 1880, volcanoes, the cooling of the earth, experiments on the elasticity of crystals, a list of Japanese minerals, stone implements in Japan, and three papers on earthquakes. From this time onwards his papers are almost all about earthquakes, and the list finished with one of very great labour, 'A Catalogue of Destructive Earthquakes, A.D. 7 to A.D. 1899,' published by the British Association in 1912.

He travelled in America and Canada; he travelled to Kamchatka, calling at most of the Kuriles (see 'Geol. Mag.,' 1879). He ventured into Korea from Siberia in 1878, when such a journey was very dangerous. He made observations in Manila, Borneo, the Australian Colonies, New Zealand, and many other islands of the Pacific. A very amusing anonymous book about Australia and New Zealand, which was frequently seen on railway book-stalls about twenty-five years ago, at once revealed the name of its author to anybody who was well acquainted with Milne; it was full of humour and fun, but the most noticeable thing was that when the author came to any town, his first visit was to whatever there might be in the way of a museum.

Milne's success was greatly due to his power to interest all sorts of people in his work. Mrs. Hoover describes its effect on a travelling visitor. But it was something much deeper which gave to him the help of scientific men. He took much interest in all scientific work, and perhaps he thought too highly of the work of other men. He was very modest as to the value of his own services to the world. He grudged no time or trouble spent in helping other people when his help, scientific, social, or pecuniary, could be of value. Both in Japan and at Shide he was very hospitable. One who lived with him in great intimacy in Japan for nearly four years puts it on record that Milne never talked scandal nor detraction, and hated to listen to such things, and he cannot remember one expressed thought or action of Milne which was ungenerous or mean. Many people gave him admiration, but his intimate friends gave him affection also.

J. P.

JAMES GORDON MACGREGOR, 1852–1913.

JAMES GORDON MACGREGOR, successor of Tait as Professor of Natural Philosophy in the University of Edinburgh, was born on March 31, 1852, at Halifax, Nova Scotia, where his father was a minister of the Presbyterian Church. His early education was obtained in his native town, and in 1871, after graduating as Master of Arts at Dalhousie College, with the highest distinction, he was elected to a scholarship which required him to pursue scientific study in Europe. With this he proceeded to the University of Edinburgh. There the present writer first met him, as a fellow student in Tait's laboratory, and at Tait's suggestion they undertook a joint research "On the Electrical Conductivity of Certain Saline Solutions," the results of which were published in 1873 in the 'Transactions of the Royal Society of Edinburgh.' The experiments dealt with solutions of zinc and copper sulphate of various strengths, and a novelty in the method was the application of the Wheatstone balance so quickly after the current was established as to escape effects of "polarisation." The measurements showed that in zinc sulphate a maximum of electrical conductivity is passed at a strength considerably short of saturation. This research, the first on which MacGregor was engaged, determined the bent of much of his later work. From Edinburgh he went on to Leipzig and continued, under Gustav Wiedemann, the study of electrolytic resistance, a subject to which he frequently returned as affording matter for further experimental enquiry or discussion. The list of his published original papers comprises about 20 items dealing with this topic or with other closely related points arising out of his earliest research.

He became a Doctor of Science of London University in 1876 and returned to Halifax to take up a position in Dalhousie College as Lecturer of Physics. After holding this for a year he resigned it for a Science Mastership at Clifton College, Bristol, and two years later, in 1879, he again returned to Dalhousie, this time as Professor of Physics in a newly established Chair which his *alma mater* was glad to offer to her distinguished son. He remained Professor there for 22 years. During that time he took an active part in forming the Royal Society of Canada, and was a frequent contributor to its 'Transactions.' The summer vacations, especially in the earlier years of his Halifax professorship, he often spent in Edinburgh, working in Tait's laboratory and keeping up a close connection with Tait himself and with the band of young physicists whom Tait inspired. In 1901 the Edinburgh chair became vacant through Tait's resignation, and, difficult as it inevitably was to find a fitting successor, those who knew MacGregor felt there was a special appropriateness in the choice which gave him control of the laboratory where he had so long been a devoted worker. MacGregor's tenure of the professorship continued for 12 years, until it was terminated by his sudden death on May 21, 1913, at the age of 61.

Prior to his appointment, the physical laboratory at Edinburgh had been little more than a museum of lecture-room apparatus, with attics giving somewhat cramped and meagre opportunity to a few students to engage in research. To triumph over material obstacles such as the lack of appliances added zest and perhaps provided a stimulus that was not without value, and there was encouragement in the reflection that it was here that the work of Leslie, Forbes, and Tait had been done. But there was no laboratory of the modern type such as forms an instrument in the education of the ordinary student. With characteristic enthusiasm MacGregor set himself to supply the want. The removal of the Department of Physics from the old University Buildings to much larger quarters, in what had been the Edinburgh Infirmary, gave him the means of making a complete transformation and creating a well equipped laboratory, which, though his plans were somewhat curtailed for lack of funds, bears testimony to the completeness of his conception and his pervading care and prevision. Later, he took up the task of collecting from old students and others money with which to establish a Professorship in Mathematical Physics as a memorial to Tait.

In 1888 he married an Edinburgh lady, Miss Marion Taylor, who survives him with one son and one daughter.

His original contributions to science deal mainly with electrical conduction, the volumes of solutions, ionisation and its effect in depressing the freezing point. In other papers he discussed the foundations of dynamics, and his studies in this matter also found expression in a text-book of 'Kinematics and Dynamics,' first published in 1887. The treatment adopted there, while following the general lines of Thomson and Tait's 'Natural Philosophy,' is in many respects original, and is distinguished from that of most text-books by the severity of its logic and its independence of assumptions. From time to time he produced addresses and articles on various questions relating to education: these also are obvious products of a mind that was clearly no slave to convention, with an outlook as wide as it was original.

Whatever MacGregor undertook he pursued with untiring industry and with a thoroughness that left no loophole for intellectual dishonesty. He was unsparing of himself in his response to anything that he accepted as a call of duty. His attention to detail was perhaps sometimes so meticulous as to obscure larger issues, or at any rate to exhaust his strength. Never robust, he was compelled at more than one stage to treat himself for long as a semi-invalid, but he faced the handicap of indifferent health with the cheerful resolution that characterised his whole attitude to life, and he overcame it sufficiently to accomplish much. An admirable teacher, he inspired his students with something of his own zeal for knowledge, his own incapacity to accept half truths. All that was best in him was put at their disposal without reserve. He had no need to make himself accessible, for he was that by nature; his cordial manner only reflected a real geniality of soul.

MacGregor was a man with many friends who will long cherish the memory of a most lovable personality. The sunny brightness of his early student days wonderfully survived into later life. It was a captivating quality, and with it there was frankness, unselfishness, insight, imperturbable good temper. He repaid friendship richly in the warmth of his own affection, in the readiness of his sympathy, in his constant willingness to help. His buoyancy stood him in good stead when, on the threshold of his career, he was warned that he had an ailment of the heart which made all effort dangerous. Though the sword did not fall then, nor till after many years, its presence must in some measure have checked his ambitions and limited his achievements. But he lived his life with a high courage, and if from time to time there was overstrain, it was of the body only: his spirit kept its elasticity to the end.

J. A. E.

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